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ELECTRON PARAMAGNETIC RESONANCE CHARACTERIZATION AND MONITORING--ETC(U)
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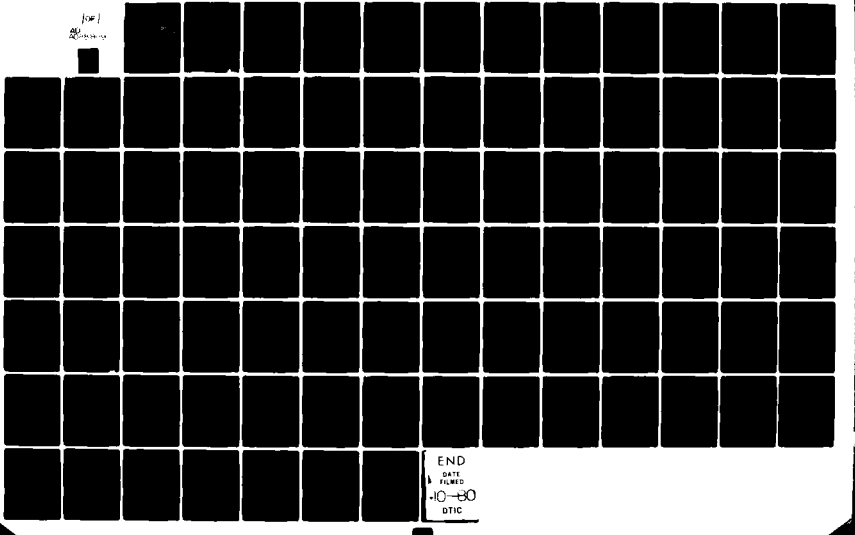

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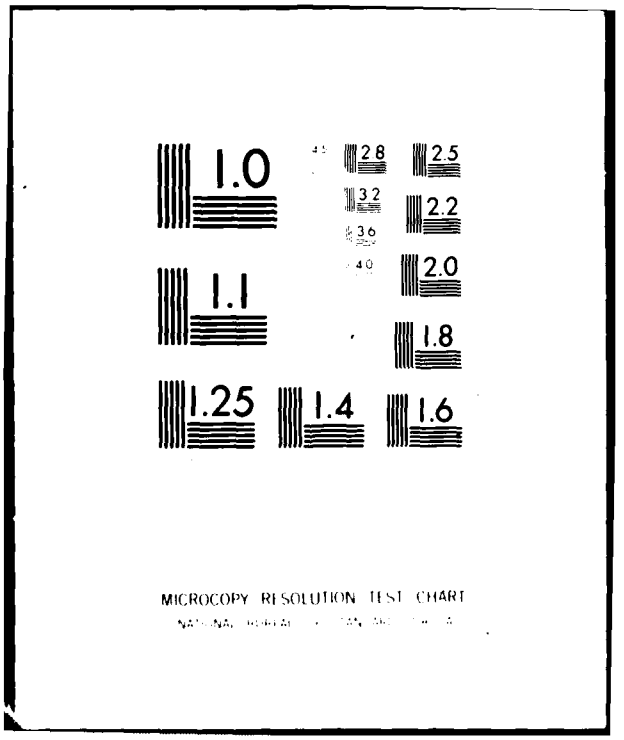
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1.6
MICROCOPY RESOLUTION TEST CHART

FINAL REPORT

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The general objective of the work reported here was to apply the Electron Paramagnetic Resonance (EPR) technique to the characterization and monitoring of impurities and dopants in silicon detector materials. The investigations were conducted in cooperation with Dr P. M. Hemenger of the AF Materials Lab (AFML)/LPO, who supplied all of the samples measured. Results have been coordinated with him and his colleagues.

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INTRODUCTION

The general objective of the work reported here was to apply the Electron Paramagnetic Resonance (EPR) technique to the characterization and monitoring of impurities and dopants in silicon detector materials. The investigations were conducted in cooperation with Dr. Patrick M. Hemenger of the Air Force Materials Laboratory (AFML)/LPO, who supplied all of the samples measured. Results have been coordinated with him and his colleagues.

Silicon is the focus of the detector materials program. The anticipated requirement for large detector arrays makes it desirable to apply the extensive technology of semiconductor devices to the infrared detector effort. The general objective for this work is to develop detectors for the 1 to 25 micrometer range. Pure silicon is limited in its response to wavelengths of 1.1 micrometers or less. In order to extend this range, impurity atoms must be incorporated into the silicon. Current dopants of interest include indium-doped silicon for response in the range of 3-5 micrometers and gallium-doped silicon for the 8-14 micrometer range. These extrinsic detectors may be used in a monolithic integrated circuit technology. The requirement that the detector array have a uniform ability to detect and respond from element to element dictates impurity uniformity and the precise control of defects. Dopant concentrations range from 10^{16} to 10^{17} per cubic centimeter, and impurity concentrations are as low as 10^{12} per cubic centimeter. This requires careful materials characterization.

The doping of silicon is achieved by introduction during growth, by thermally controlled diffusion, or by ion implantation. The electrical properties, the time response of the device, its operating temperature, and its optical sensitivity are affected by the presence of impurities. To optimize these characteristics of the detector, careful measurements of optical and electrical properties must be made as a function of temperature. Optical properties of interest include spectral absorption, photoluminescence, and photoconductivity. The electrical transport properties, primarily resistivity and Hall effect, are the responsibility of Dr. Hemenger. With these measurements various detector materials are characterized, including the influence of processing methods such as thermal treatment, ion implantation, or transmutation doping.

The performance of silicon infrared detectors is dependent on starting material quality. The degree of purity of the crystal depends on the method of growth. The work summarized in this report includes samples grown by the Czochralski method in quartz crucibles and by vacuum multiple float zoning. The float zoning method in general is more attractive because of lower impurity concentrations.

Undesired and often unknown defects have a negative effect on the properites of detectors. These often result from crystal growth or detector fabrication. Heat treatment during processing of the detector, or annealing of ion-implanted or neutron-transmuted material may cause a redistribution of necessary dopants, or may introduce unknown and undesired centers. The EPR technique has been employed[1] in the identification of various defects in silicon, and thus its use in this project.

EXPERIMENTAL

In this study a total of 55 silicon samples were investigated via EPR measurements. Included were crystals doped with Boron, Gallium, or Indium, as well as some without intentional doping. Some were electron irradiated; some were annealed. Details follow.

1. Samples

In Table 1 is given a listing of the samples examined, along with intentional dopants and treatments. All were single crystals in wafer form in the neighborhood of half a millimeter thick. Concentrations were inferred from Irvin's p-type resistivity curve.

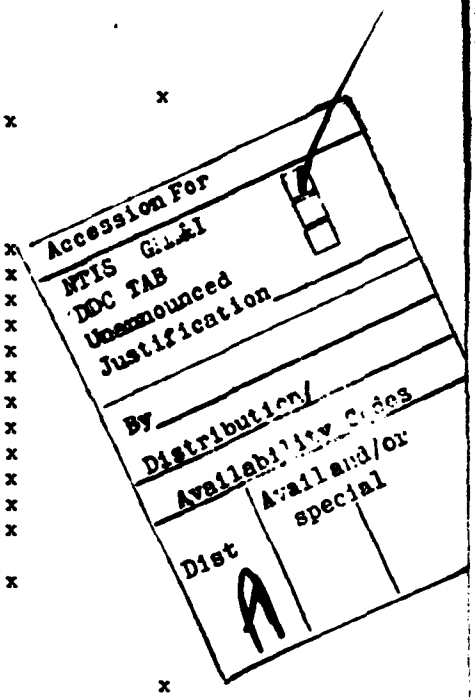
2. Equipment

The device that was used in the study is a modified form of the Varian Associates Model 4500 series EPR Spectrometer. This x-band spectrometer operates at about 9.5 Gigahertz, or about 9.2 Gigahertz with a quartz dewar inserted. The external magnetic field for the Zeeman splitting is provided by a Varian 12-inch regulated and water-cooled magnet with field scanning provisions. The microwaves are produced by a klystron, are distributed by a microwave bridge, and are detected by a crystal detector. The original hybrid tee bridge has been replaced by a more efficient three-port-circulator arrangement. The klystron is stabilized with automatic frequency control. The spectrometer currently operates in the absorption mode.

This spectrometer has a 100 kilohertz crystal controlled oscillator which generates the field modulation frequency, and a high gain amplifier and phase detector for detection of the EPR signal.

Table 1 SAMPLES EXAMINED

SAMPLE NUMBER	AIR FORCE MATERIALS LABORATORY NUMBER	DOPANT	AS GROWN MEASUREMENT	ELECTRON IRRADIATION	ISOCHRONAL ANNEAL	ISOTHERMAL ANNEAL
1	3605	-	x			
2	3605	-	x			
3	GZ-185	In	x		x	
4	DC 002-#18	In	x			
5	GZ 163-26	In	x			
6	001-005-xxxx	In	x			
7	W-NTD	P	x			
8	001-011-WG 004 #60	In	x			
9	W-NTD	P	x			
10	W-NTD	P	x			
11	001-011-xxxx	P	x			
12	034-131-0046	Ga	x			x
13	050-155-0044	In	x		x	
14	050-151-0045	In	x			
15	0024.5	In	x			
16	0023.5	In	x			
17	032-119-0098	B	x			
18	3605	-	x		x	
19	3605	-	x		x	
20	NTD-2	P	x		x	
21	011-219-0245	In	x	x	x	
22	011-219-0246	In	x	x	x	
23	011-223-0247	In	x	x	x	
24	011-223-0248	In	x	x	x	
25	011-224-0249	In	x	x	x	
26	011-224-0250	In	x	x	x	
27	011-228-0251	In	x	x	x	
28	011-228-0252	In	x	x	x	
29	011-228-0253	In	x		x	
30	011-223-0247	In	x			
31	131-368-0412	Ga	x		x	
32	132-369-0413	Ga	x			
33	133-370-0414	Ga	x			
34	130-365-0415	B	x			
35	130-366-0416	B	x			x
36	130-367-0417	B	x		x	
37	129-362-0418	B	x			x
38	129-363-0419	B	x		x	
39	129-364-0420	B	x			
40	3605	-	x			x
41	NTD-2	P	x			
42	001-009-0411	In,B	x			
43	3605	-	x		x	
44	3605	-	x		x	
45	034-131-0478	Ga	x			
46	1202	-	x		x	
47	1202	-	x			x
48	4802-3	-	x		x	
49	4802-3	-	x			x
50	032-119-xxxx	B	x		x	
51	032-119-xxxx	B	x			
52	032-119-xxxx	B	x			x
53	011-223-0248	In	x			x
54	032-199-xxxx	B	x			
55	032-199-xxxx	B	x			



Without signal averaging the spectrometer can detect $10^{12} \pm 25\%$ spins. Due to the weak intensity of the EPR lines observed in silicon, a signal averaging technique was employed. Two units have been used: a Varian C-1024 Time Averaging Computer, and a Tracor Northern TN-1710. Both yielded spectra with adequate signal-to-noise ratios.

3. Treatments

In this study some samples were electron irradiated. The irradiations were done at room temperature on a 1 MeV Van de Graaff accelerator with electron fluences ranging from 10^{15} to 10^{17} electrons per square centimeter. The samples were exposed from both sides of the wafer. All irradiated samples were maintained at liquid nitrogen temperature until the first EPR measurements.

Many of the samples were annealed. The heat treatment was done in a Blue M Stabil-Glow tube furnace with temperature control. The samples were on a quartz boat in a quartz tube and were bathed in an argon atmosphere during heating and cooling. The samples were sandwiched between ultra-high purity silicon wafers during treatment. The furnace was brought to temperature before the boat was inserted. At the end of the anneal time, the boat was quickly pulled to the end of the quartz tube and kept in the argon atmosphere until its return to room temperature. All samples were given an RCA wash cycle before each anneal and were measured by EPR just afterwards.

When isochronal anneals were done, the time at temperature was one-half hour and the temperatures range in 100 degrees steps from 250°C to 750°C or 1050°C. The isothermal anneals were performed at 550°C for total times ranging from one-half hour to 16 hours.

4. Measurements

For the EPR measurements signal averaging was employed. Typically 25 sweeps produced a useful spectrum. For magnetic field calibration and intensity calibration, a manganese marker was permanently installed in the EPR cavity. The marker employed was forsterite, a material characterized[2] earlier by the principal investigator. Its location in the cavity was such that its phase was opposite to that of the sample, making differentiation easy. The marker has a six line hyperfine spectrum which spans some 435 gauss centered near g = 2. Lines three and four were used for g-value measurements, and intensity measurements were made relative line three.

Both g-value and intensity calibrations were made relative to a standard reference of 0.00033% pitch in KCl.

5. Related Measurements

At AFML Dr. Hemenger and his colleagues are involved with measurements of Hall effect, resistivity, spectral absorption, photoluminescence, and photoconductivity. Where possible, the EPR measurements were coordinated with the above, mostly Hall effect and resistivity.

OBSERVATIONS

The thrust of this project was divided into two parts, one specific project and a second more general one. The first was a study of indium-doped silicon and was an attempt to aid in the understanding of the so-called "X-level." This understanding is very important to the development of detectors for the 3-5 micrometer range. The second part was a more general study of defects in silicon detector materials using Electron Paramagnetic Resonance.

1. Si:In X-level

The study of indium-doped silicon for use as a detector in the 3-5 micrometer range has led to an interesting puzzle, the identity of the "X-level." A new acceptor level located at 0.111 ± 0.002 eV from the valence band has been observed[3] in indium-doped silicon. It is believed to be in all Si:In samples except when masked by overcompensation. The existence of this level with an ionization energy significantly less than that of In, 0.156 eV, reduces the maximum temperature for background-limited performance. The usual method of eliminating the effect on low temperature behavior by overcompensating the shallow impurity center is undesirable here due to the degradation in photoconductive properties that would result. Identification of and control of this defect is obviously needed.

In order to explore this problem an EPR study was initiated in cooperation with Dr. Hemenger and his colleagues. It was a coordinated effort that combined EPR, Hall effect, photoluminescence, absorption, and photoconductivity measurements to study the effect of electron irradiation on In-doped silicon. Samples of Si:In and wafers of high purity silicon were used. The experimental samples included eight EPR samples, four Hall samples (van der Pauw configurations also used for photoconductivity), four luminescence samples, and two absorption samples. All of the Si:In samples were cut from the same boule.

To achieve a variation in the measured concentration of the X-level defect, the technique of electron irradiation was used. Four fluences of electrons were used to seek a relationship between the concentration of X and the fluence. Isochronal annealing of the samples followed the irradiations.

Electron irradiation of Si:In has been observed[4,5,6] to change the apparent concentrations of residual impurities, as measured by Hall effect, as well as the concentration of the major dopant. This combined study was initiated to extend these findings. Since the time frame available for the EPR study was considerably shorter than that for the rest of the study, two sets of EPR samples were irradiated. One set was annealed immediately, while the other set have been annealed along with the samples for the other measurements. As of this writing, that set of anneals has progressed to 550°C. Both sets of anneals were done in an identical fashion. The first set of samples have been through two complete anneal cycles, and a control sample through a third. These results are summarized in two papers that have been presented and which are reproduced in Appendices A and B. The data does not suggest observation of the x-level, but at least two other possibilities are identified in the Appendix B paper. They are an aluminum-interstitial/aluminum-substitutional complex (G-20 spectrum) and a P1-center, a pentavacancy cluster. Also there is some evidence of a line corresponding to dangling bonds. It is useful to note that, where the transport studies have been completed, it was necessary to include an aluminum impurity to fit the data. Also it should be noted that ordinarily EPR spectra is not observed from acceptor dopants in silicon in the absence of externally applied stress.

At this point in time it is not possible from EPR alone to identify clearly the center or centers responsible for the observed spectra in electron-irradiated Si:In. Confirmation awaits completion of the transport work at AFML. Interaction will continue.

2. Silicon Defects

EPR studies in silicon damage have been particularly successful, as demonstrated by the early series of papers[7,8,9,10,11] by Watkins and co-workers. Various reviews[12,13,14] of the subject have appeared over the years.

Ion implantation is a useful technique for introducing dopants into the silicon crystal. In the process, ions of a particular impurity element, such as boron or phosphorus, are shot from an accelerator into a crystal such as silicon. The choice of the injecting energy determines the depth to which the silicon is doped. However, two major problems limit the desirability of ion implantation. The bombardment with high-energy ions disrupts the orderly arangement of the crystal lattice giving much surface damage. In addition the ions do not all settle in substitutional lattice sites to become donors or acceptors. This damage lends itself to study by EPR.

Several boron-implanted silicon samples were examined along with some conventionally doped Si:B. Significant differences in spectra were not observed either in the as-grown state or after annealing. Details are given later in this section.

A useful process for donor doping is neutron transmutation doping. The process is based on converting ^{30}Si to ^{31}Si by an (n, γ) reaction via thermal neutrons from a reactor. The ^{31}Si

decays by negative beta decay to ^{31}P, the impurity sought. The donors produced are distributed uniformly throughout the lattice. Also the rate of production of dopant can be carefully controlled. These two major advantages of neutron transmutation doping are offset somewhat by the radiation damage effects that occur during the radiation. Several neutron transmutation doped samples were examined during this study. The details on one of them are given in the paper in Appendix C.

a) Dopant Survey

The main thrust of this part of the study included a survey of samples with a variety of dopants. They included two boron, one implanted and one conventional, one gallium, one indium, one phosphorous via neutron transmutation doping, and one undoped sample. The details of the as-grown measurements and the isochronal annealing studies are given in the paper reproduced in Appendix C. There it is clear that the four acceptor-doped samples all have a line near the g-value for dangling bonds before anneal. After anneal, each has a line, or lines, with lower g-values; in fact, these values are near that of the neutron transmutation doped sample. The undoped sample showed no line in the as-grown state, but acquired a line with the lower g-value upon anneal in 100°C steps. However, for comparison, another piece of the same wafer of undoped material treated only to one half-hour anneal at 550°C, exhibited no line afterwards. This same result was repeated later with another pair of samples from the same wafer.

In that paper the change in magnetic field location of the observed line and hence the inverse change in g-value is detailed. There it is concluded that the most likely sources of the line, or lines, are dangling bonds and the P1, or pentavacancy, center.

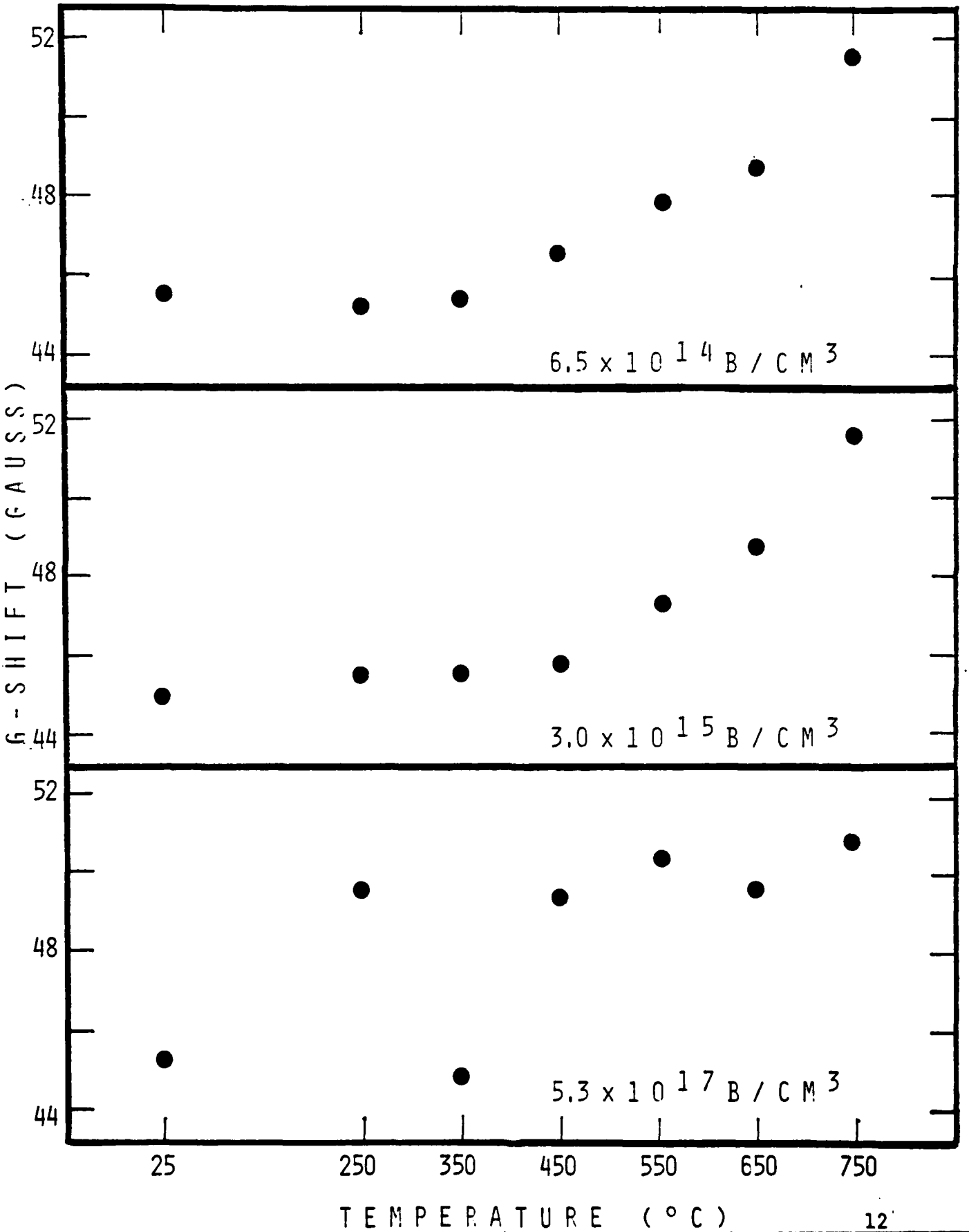
b) Boron Concentration Study

Since significant boron impurity concentrations are present in most silicon detector materials, a more detailed investigation of Si:B was undertaken. Three samples from each of three boules with different boron dopant concentrations were used. Each was measured in the as-grown condition. From each trio, one was annealed isochronally and another isothermally.

The as-grown samples each exhibited a line with a g-value of 2.0059 ± 0.0002. The relative intensity of the line decreased slightly as the boron concentration increased. (For concentrations per cm^3 of 6.5×10^{14}, 3.0×10^{15}, and 5.3×10^{17}, the relative intensities were 1.00, .73, and .51). During the isochronal annealing treatment, the shift in magnetic field location of the line was monitored. For the three concentrations, this information is plotted in Figure 1. Notice that the increase in field location (as measured from the third line of the manganese marker), and corresponding reduction in g-value, is almost identical for the two lower concentration samples. The change is much less orderly for the higher concentration sample. There is, however, a rather common lower limit on g for the three around 2.0024, corresponding to the maximum g-shift on each graph.

For contrast to the above temperature variation of g, an isothermal anneal was conducted at 550°C, where many of the intensity

FIGURE 1


52
48
44
6.5 x 10 14 B / C M 3
52
48
44
3.0 x 10 15 B / C M 3
52
48
44
5.3 x 10 17 B / C M 3
G - SHIFT (GAUSS)
25
250
350
450
550
650
750
TEMPERATURE (°C)

vs. temperature curves peaked. These results for the three concentrations are shown in Figure 2. The curves for the three concentrations are quite similar, each starting at about g = 2.0059 and saturating around g = 2.0025. Each curve had saturated after a total anneal time of two hours. The intensity of the line during this isothermal anneal varied in a strange way. As seen in Figure 3, it increased rapidly during the first hour, then dropped abruptly thereafter. It appears that the defect responsible for the line grew as some other defect annealed out, and then rapidly annealed out itself.

The shift in g-value in these samples appears to support the theory that there are at least two lines present, and that their relative intensities vary, shifting dominence from one to the other upon treatment.

c) Gallium Concentration Study

Due to the desirability of gallium doping for extending the infrared detection range, a similar study was initiated for Si:Ga. Samples with four different gallium concentrations were used and compared to some undoped silicon samples. Similar to the Si:B samples, a line was observed in each in the as-grown condition. (For concentrations per cm^3 of 8.0×10^{14}, 1.7×10^{15}, 6.0×10^{15}, and 1.5×10^{17}, the relative intensities were 1.00, .66, .97, and 1.45). During isochronal anneal, the intensities presented in Figure 4 were observed. The data nicely fits a quadratic expression. For the same crystal the g-shift was monitored as reported in Figure 5. Its shape is very similar to that of the high concentration Si:B. It also shifts from some 2.0059 as grown to a saturated value around 2.0024. This also suggests at least two lines.

FIGURE 2

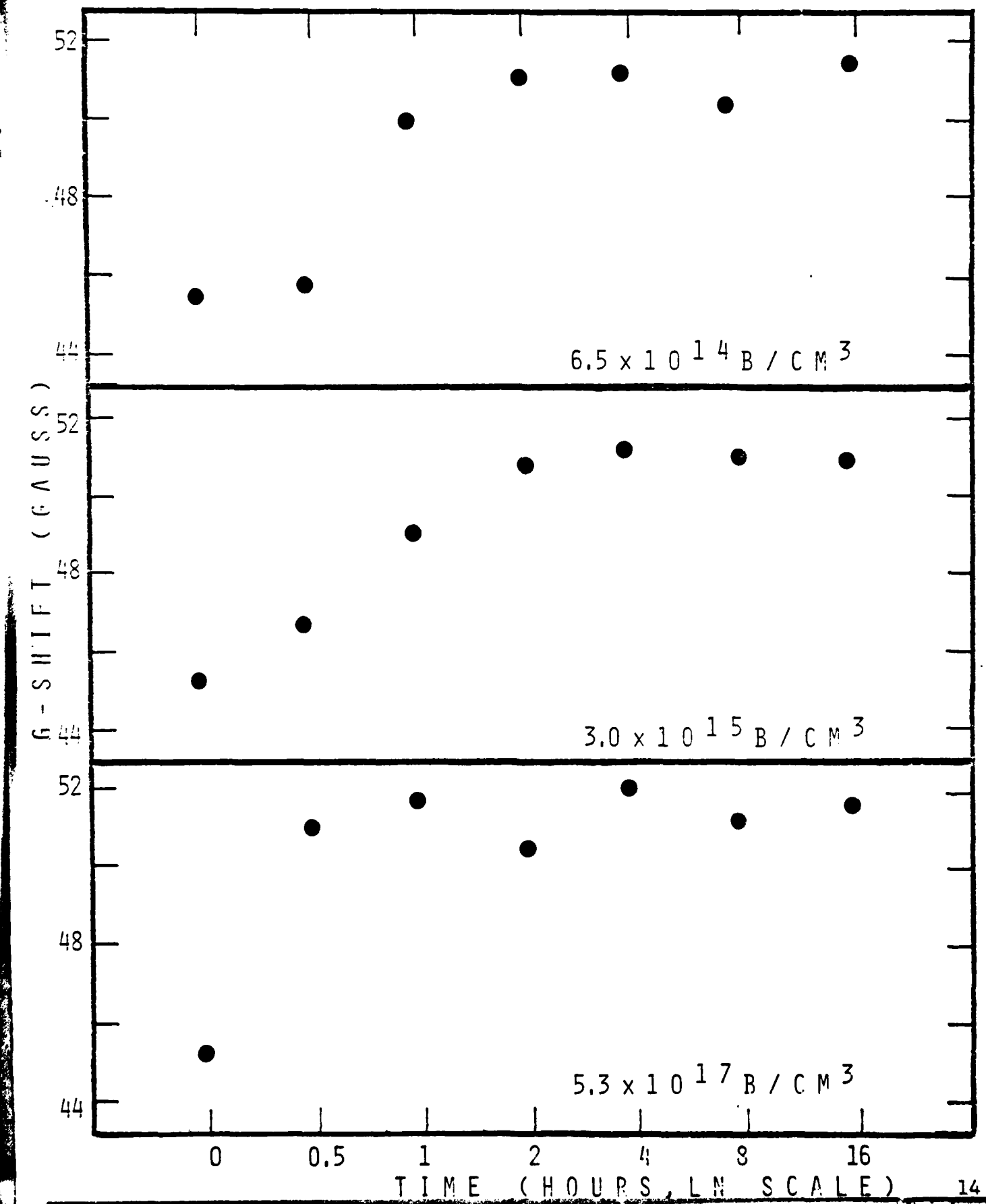

52
48
44
6.5 x 10 14 B / CM 3
52
48
44
3.0 x 10 15 B / CM 3
52
48
44
5.3 x 10 17 B / CM 3
G - SHIFT (GAUSS)
0
0.5
1
2
4
8
16
TIME (HOURS, LN SCALE)

FIGURE 3

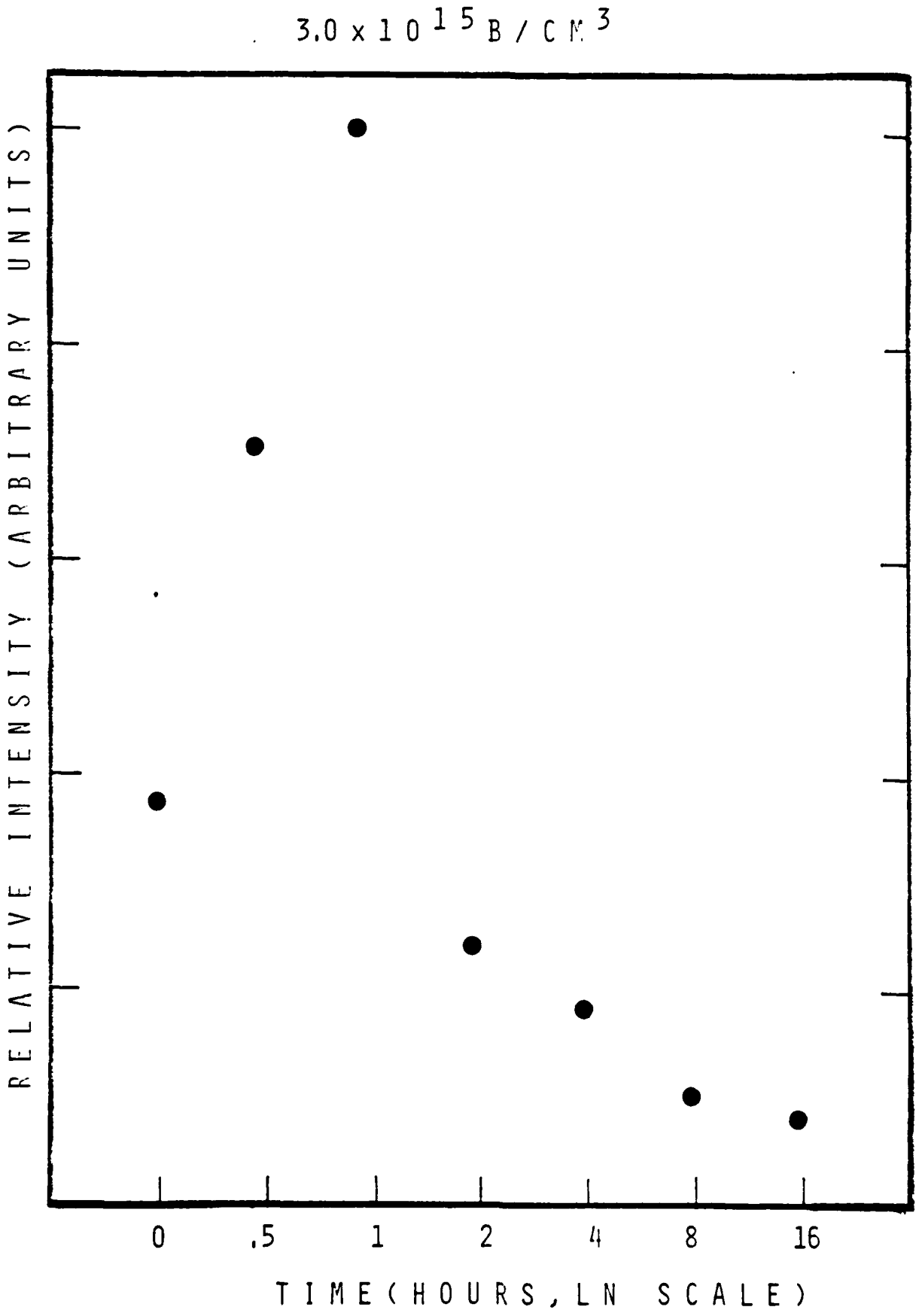

3.0 x 10 15 B / CM 3
RELATIVE INTENSITY (ARBITRARY UNITS)
0
.5
1
2
4
8
16
TIME(HOURS, LN SCALE)

FIGURE 4

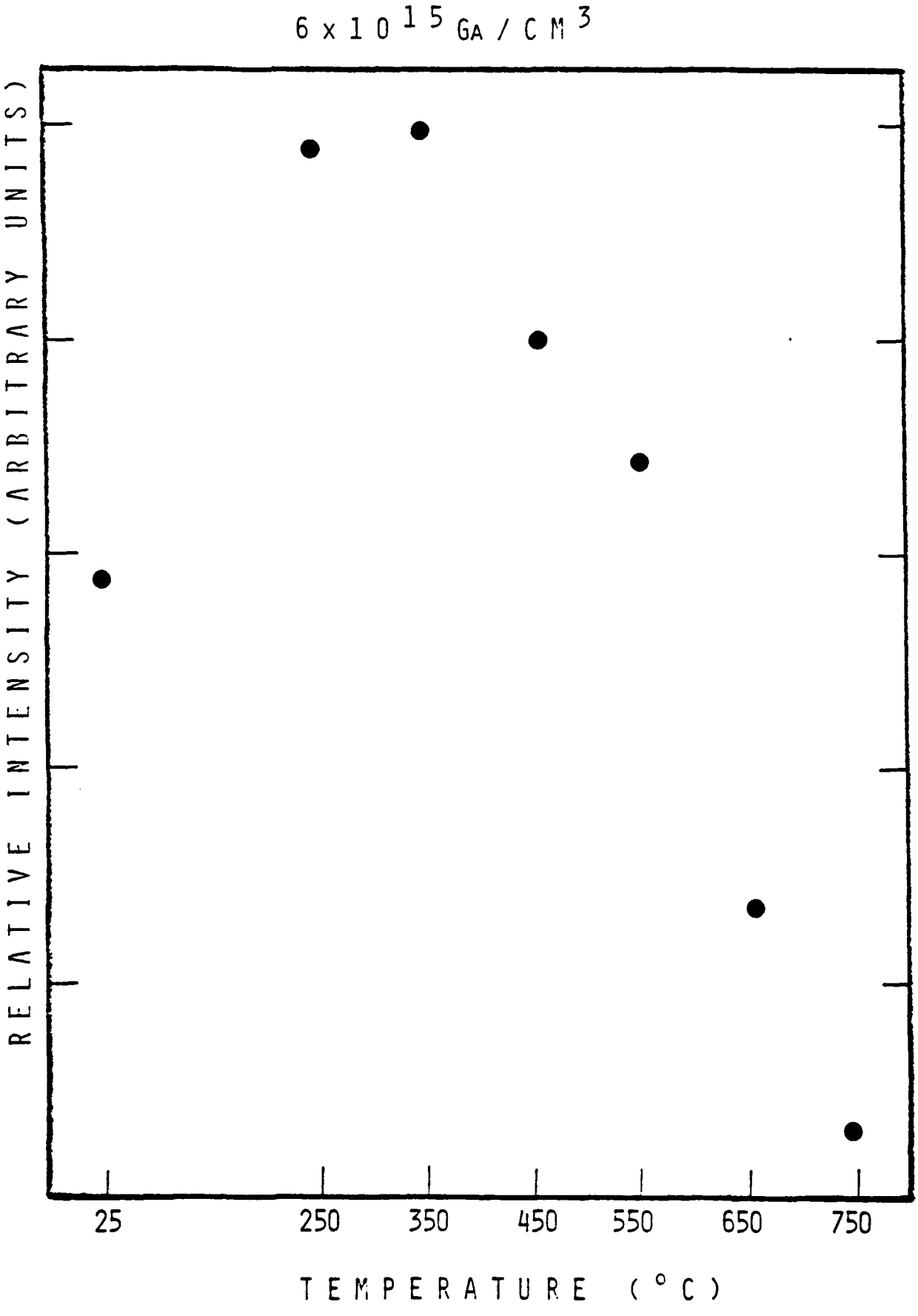
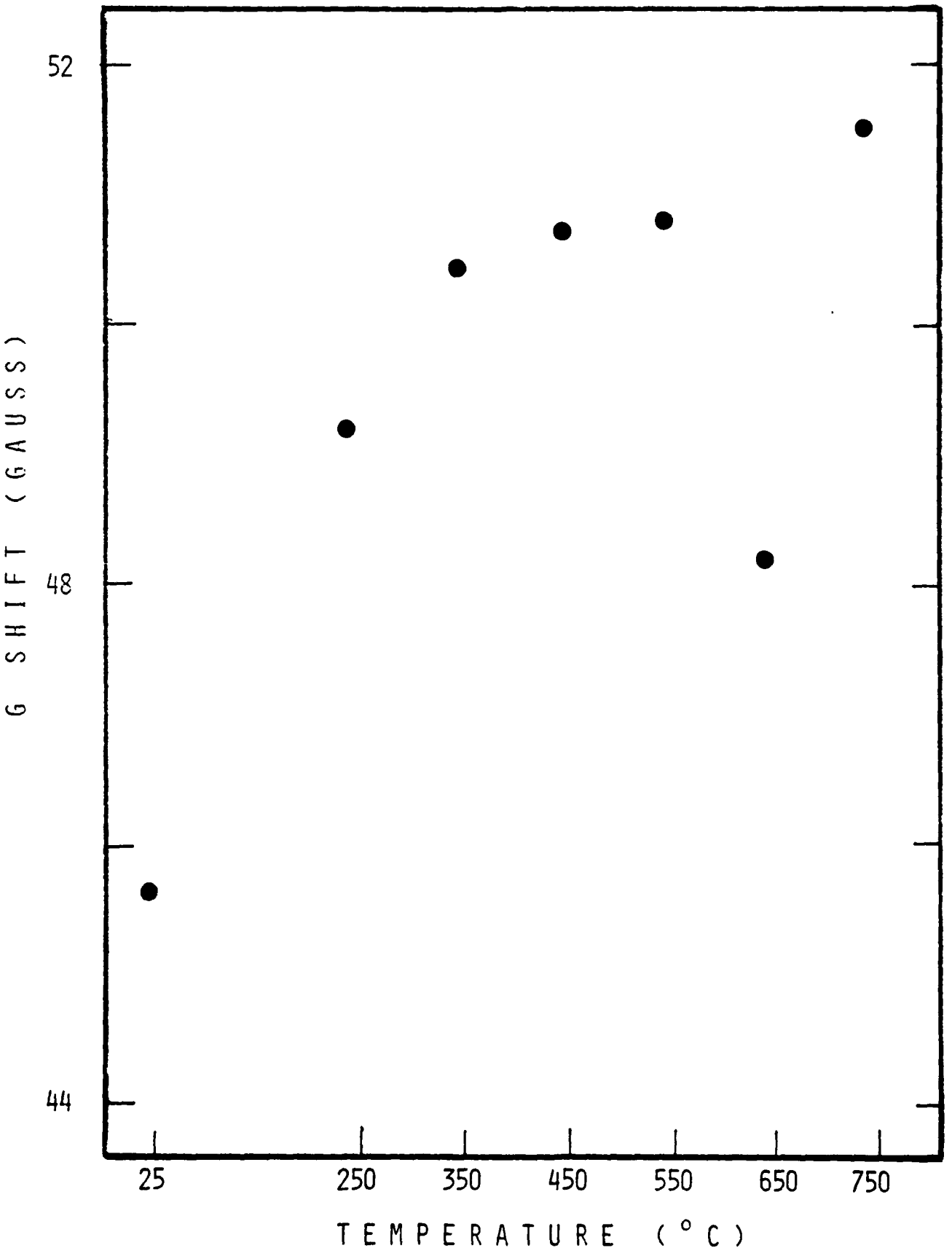

6 x 10 15 GA / CM 3
RELATIVE INTENSITY (ARBITRARY UNITS)
25
250
350
450
550
650
750
TEMPERATURE (°C)

FIGURE 5


6 x 10 15 GA / C M 3
52
48
44
G SHIFT (GAUSS)
25
250
350
450
550
650
750
TEMPERATURE (°C)

For comparison an undoped silicon sample was isochronally annealed in a similar manner. Its graph, plotted in Figure 6, is quite similar to that of Si:Ga. It also can be fit to a quadratic. While its shape is quite similar, its maximum height is just about half of that of Si:Ga. For the undoped crystal, the g-value was also monitored during the ischronal anneal. As shown in Figure 7, it is quite similar to Si:Ga. In order to gain more information on the shift from "high" g to "low" g, an isothermal anneal was conducted on this sample. The result, shown in Figure 8, is very similar to earlier plots, with the g downshift occuring in the first half-hour. Once again, there is strong evidence for at least two lines due to two defects, with the relative intensities varying independently with treatment.

d) Survey of g-values

From the variety of measurements made and reported in this report, a general pattern has emerged with respect to g-values. It appears to hold in over ninty-five per cent of the g-value measurements. A variety of values is listed in Table 2, where all measurements taken from 250 gauss sweeps are reported. Many other measurements were also taken on 100 gauss sweeps. However, these are not as accurate, although there is good general agreement with those listed in Table 2. From that table it is obvious that almost all as-grown measurements yield a g-value near 2.0059. On the other hand, samples that have been electron irradiated, neutron bombarded, or heat treated, have lower g-values, mostly near 2.0024. It appears that there are at least two lines, on with "high" g-value and the other with "low" g-value, corresponding to the two extremes. Intermediate g-values probably result from a mixture when the two intensities are similar and the lines not properly resolved.

FIGURE 6

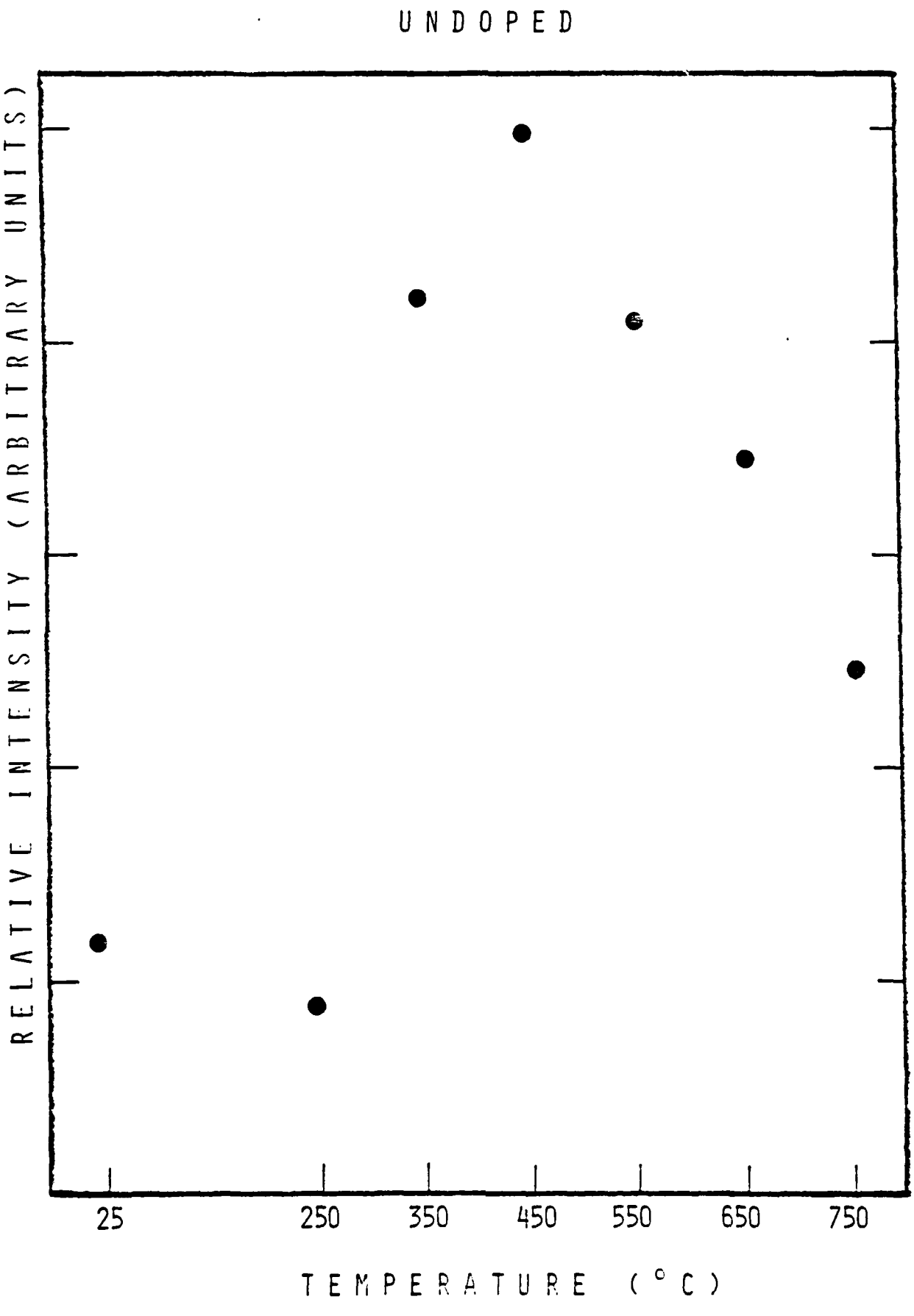

UNDOPED
RELATIVE INTENSITY (ARBITRARY UNITS)
25
250
350
450
550
650
750
TEMPERATURE (°C)

FIGURE 7

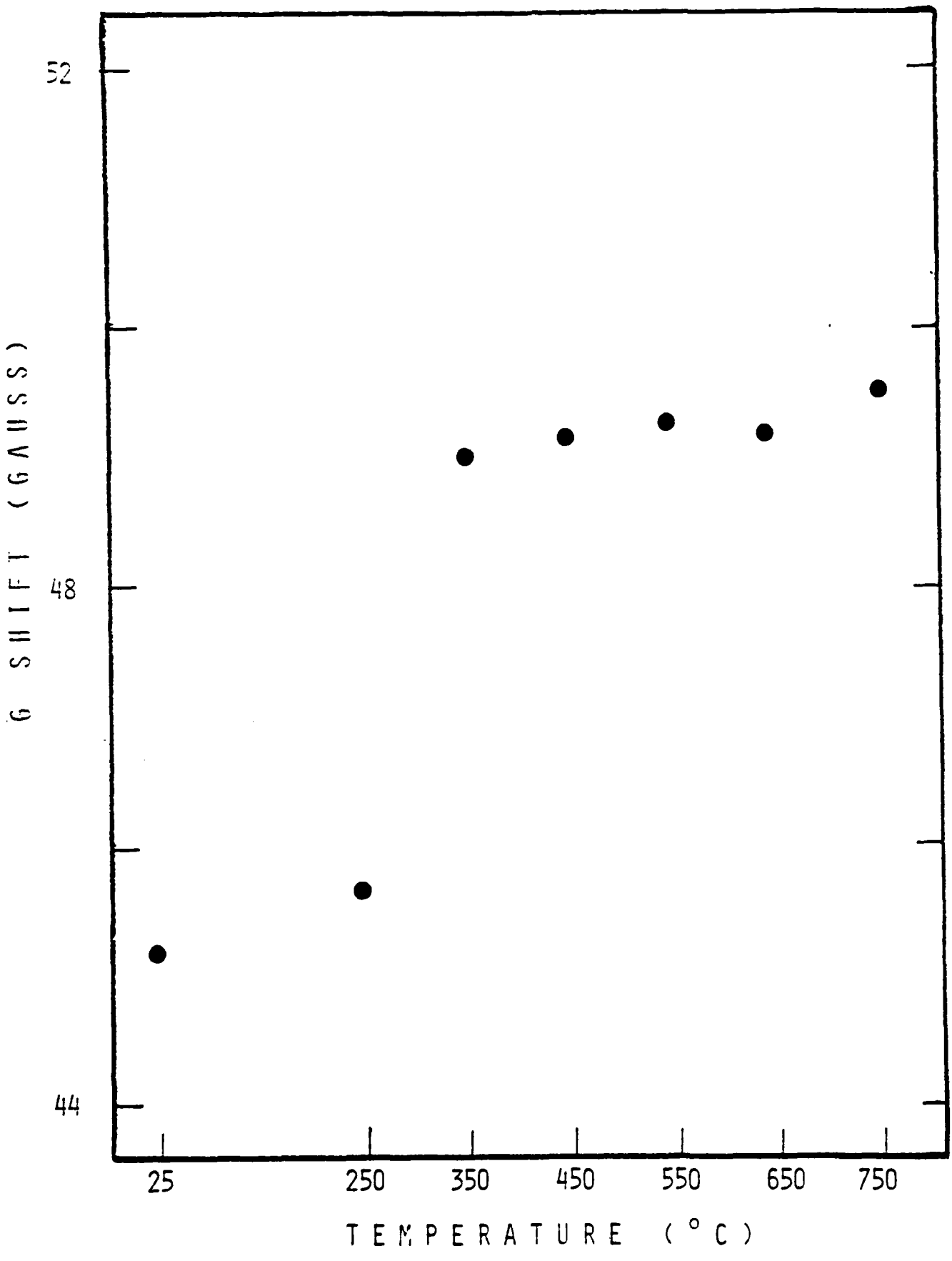

UNDOPED
52
48
44
G SHIFT (GAUSS)
25
250
350
450
550
650
750
TEMPERATURE (°C)

FIGURE 8

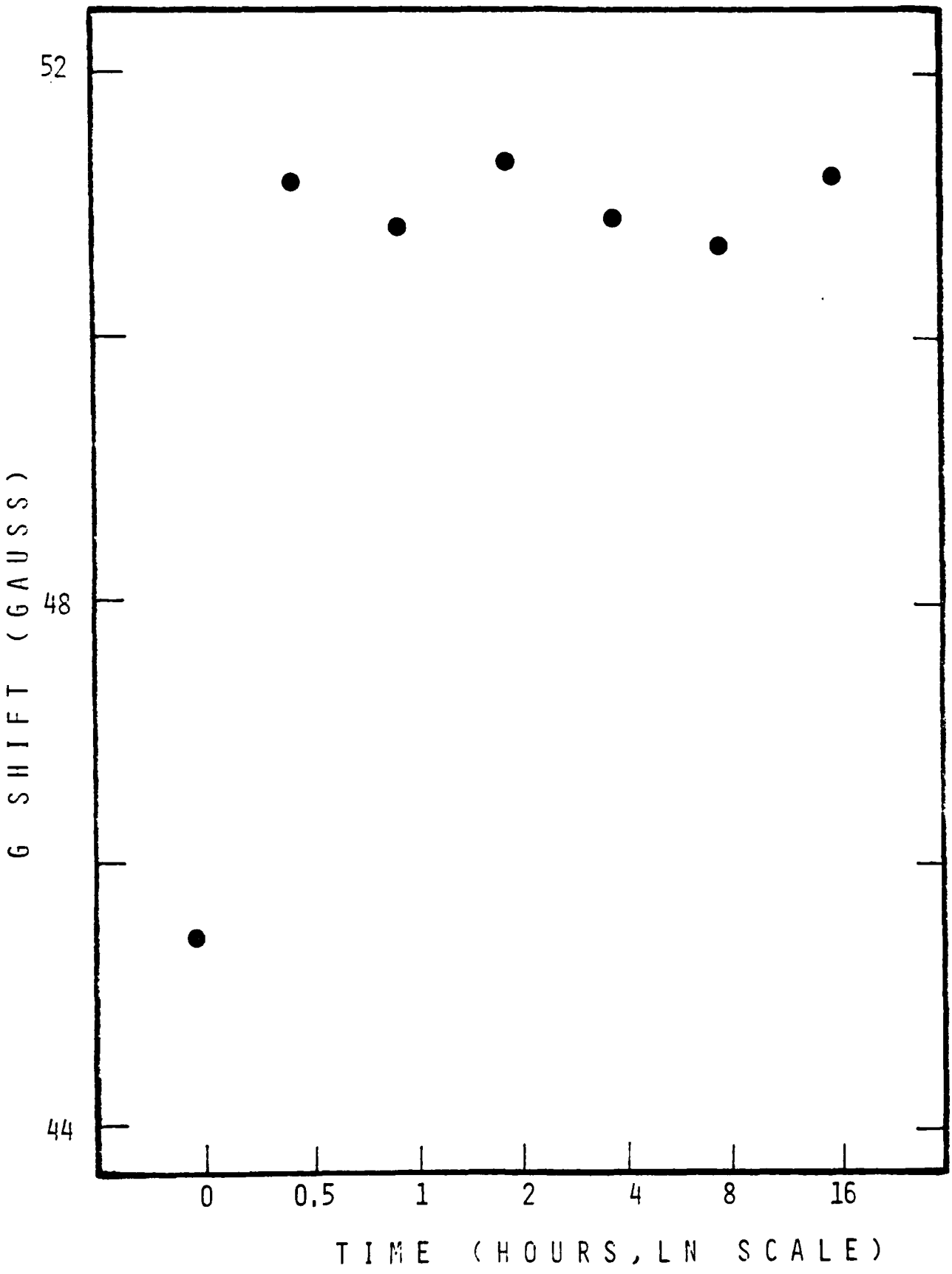


Table 2 SELECTED G-VALUES

SAMPLE NUMBER	DOPANT	TEMPERATURE (°C)	TIME (MINUTES)	G-VALUE (±0.0002)
3	In	550	30	2.0028
3	In	650	30	2.0032
3	In	750	30	2.0027
12	Ga	0	0	2.0061
13	In	550	30	2.0029
13	In	650	30	2.0026
13	In	750	30	2.0024
18	-	750	30	2.0032
19	-	550	30	2.0028
19	-	650	30	2.0036
20	P	550	30	2.0027
20	P	650	30	2.0026
20	P	750	30	2.0037
20	P	750	30	2.0033
21	In	750	30	2.0039
27	In	750	30	2.0045
29	In	550	30	2.0029
29	In	650	30	2.0030
29	In	750	30	2.0023
31	Ga	0	0	2.0060
31	Ga	550	30	2.0032
31	Ga	750	30	2.0028
36	B	0	0	2.0062
36	B	550	30	2.0025
36	B	750	30	2.0020
37	B	0	0	2.0061
38	B	0	0	2.0052
38	B	550	30	2.0027
38	B	750	30	2.0023
42	In,B	0	0	2.0059
44	-	750	30	2.0047
46	-	0	0	2.0060
47	-	0	0	2.0057
48	-	0	0	2.0040
49	-	0	0	2.0024
50	B	0	0	2.0036
52	B	0	0	2.0057
53	In	0	0	2.0076
53	In	550	60	2.0036

SUMMARY

All of the evidence gathered in this project points to a conclusion that at least two, and possibly more, room temperature EPR lines of very low intensity are observed in silicon. In the as-grown samples g = 2.0059; after electron or neutron irradiation or annealing treatments, a line with about g = 2.0024 grows to a large intensity around 550°C. The line in the virgin material appears in boron, gallium, or indium doped material or in undoped material. Since the g-value is essentially the same in all, this suggests some inherent defect in silicon such as dangling bonds. Reports[15,16] of such observations have been made recently.

Electron[17] and neutron[18] irradiation introduce a variety of defects. Some that are important from 150 to 350°C are the phosphorus/vacancy complex (E-center), the oxygen/vacancy complex (A-center), and the divacancy. Others include G-20 and P-1. Aluminum complexes are an attractive possibility,[19] and the transport studies done in cooperation with this project are consistent with that possibility.

From this study one can tell the general types of defects to be found in silicon detector materials. It is now clear that a more sophisticated approach to spectral analysis is needed, perhaps computer simulated spectra. Such a study along with the future results of the transport and optical studies in progress at AFML could lead to precise determination of the defects involved.

PRESENTATIONS

The Electromagnetic Materials Division of the Air Force Materials Laboratory has a Laser and Optical Materials Branch. This branch has an infrared detectors project via WUD#-8. During the course of this project the Principal Investigator regularly attended the monthly WUD meeting. On four occasions he gave that group presentations on this work.

To this point in time, three papers on this work have been presented at professional meetings of the American Physical Society. Two more are planned for this Fall. The first three are reproduced and referenced in Appendices A, B, and C. The remaining two are outlined in the text. The titles are:

1) "An EPR Study of Electron-irradiated Indium-doped Silicon." (Appendix A).

2) "An Annealing Study of Indium-doped Silicon after Electron Irradiation." (Appendix B).

3) "EPR Measurements in Silicon Doped with Boron, Gallium, or Indium Acceptors." (Appendix C).

4. "An Annealing Study of Boron-doped Silicon via EPR" (Observations, Section 2b).

5. "EPR in Silicon as a Function of Dopant Gallium Concentration." (Observations, Section 2c).

It is anticipated that the entire project will be summarized in a later journal article.

ACKNOWLEDGEMENTS

The Principal Investigator wishes to acknowledge the interaction with and the helpfulness of Dr. Patrick Hemenger of AFML/LPO. Also Steven Smith and Dr. Melvin Ohmer, General Manager of WUD #48, and the other members of WUD #48 were most helpful. The careful assistance of John Meder in the taking of data was invaluable in this project. Useful interaction with faculty colleagues, Dr. Thomas Graham and Dr. Rex Berney, and the support of the Department Chairman, Dr. James Schneider, is greatly appreciated.

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APPENDIX A

Abstract Submitted

for the Fall Meeting of the

Ohio Section of the American

Physical Society

November 2-3, 1979

Reference: Bulletin of the American Physical Society 25, 461 (1980)

An EPR Study of Electron-irradiated Indium-doped Silicon.* J.N. MEDERT and G.R. MINER, Univ. of Dayton Physics Department and S.R. SMITH, Univ. of Dayton Research Institute.--We present a preliminary report of electron paramagnetic resonance measurements on 1 MeV electron-irradiated indium-doped silicon. Four fluences ranging from 10^{16} to 10^{17} electrons per square centimeter were employed. A resonance line near g=2 observed at room temperature and at 77 K in unirradiated samples was altered in intensity by electron bombardment. Some possible models will be examined.

*Supported in part by USAF Office of Scientific Research and USAF Materials Laboratory.
†NSF Undergraduate Research Participant.

"An EPR Study of Electron-irradiated Indium-doped Silicon"

We would like to present preliminary results of electron paramagnetic resonance (or EPR) measurements on one-MeV electron irradiated indium-doped silicon. The experiment was initiated because of reports by Swaminathan, Lang, Hemenger and Smith that the transport properties of indium-doped silicon were altered by electron irradiation. In their work they reported the observance of an unknown level, also seen by others, and generally referred to as the x-level. That group and other coworkers have now set out to perform additional measurements that include optical and transport studies. The present EPR study is coordinated with these experiments.

All the samples investigated in these experiments were cut from a single boule of Float-zone indium-doped silicon. The EPR samples were cut into wafers about one-half of a millimeter thick and had a mass in the neighborhood of 50 milligrams. A total of ten samples were studied. The treatment of the samples is shown in the first slide. (1) Two each were irradiated at each of four electron fluences ranging from 10^{16} to 10^{17} electrons per square centimeter. The remaining two samples served as controls, one of which has annealed with the irradiated samples. The irradiations were done on a 1 MeV Van de Graaff accelerator with the samples exposed from both sides of the wafer. All irradiated samples were maintained at liquid nitrogen temperature until the first EPR measurements.

The samples were oriented so that the [100] - direction was along the magnetic field. The spectrometer used was an x-band Varian Model 4500 Series. Due to the weakness of the signals at room temperature and at liquid nitrogen temperature, signal averaging was employed. Reasonable signals for most samples were collected in 25 sweeps. For the measuring of g-values and relative intensities, a manganese marker was permanently installed in the cavity. The next slide (2) shows that its location

was such that the phase of its EPR line was opposite to that of the unknowns. The marker has a line approximately 50 gauss down field from the observed silicon line near g = 2 and was used for monitoring. The separation in gauss between the reference line and the sample line could be measured accurately. Also the height of the reference line was used in the measure of relative intensity.

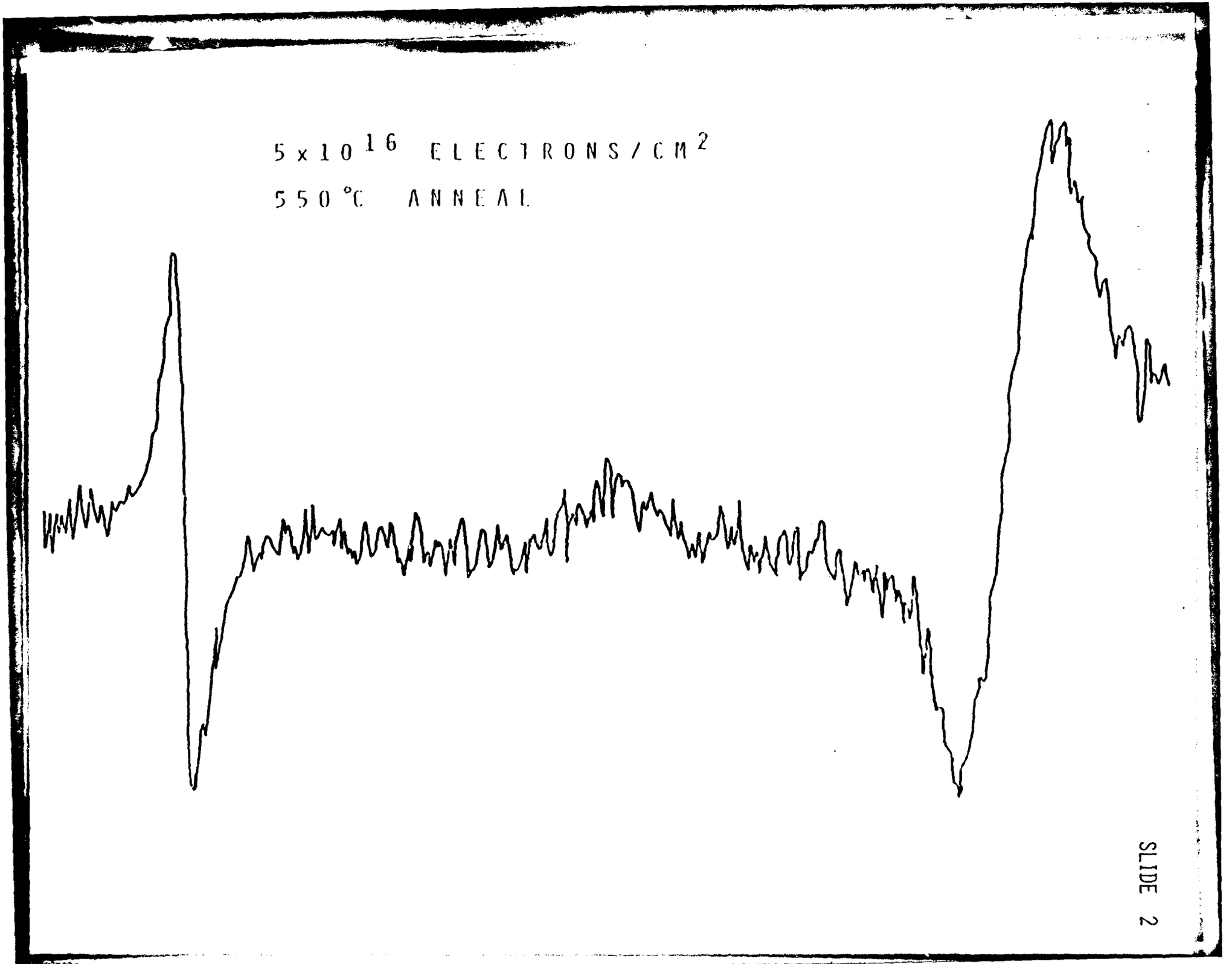
The annealing was done in a furnace with temperature control as shown in the next slide (3). The samples were on a quartz boat in a quartz tube and were bathed in an argon atmosphere during heating and cooling. The samples were sandwiched between ultra-high purity silicon wafers during anneal as pictured in the next slide (4). Only half of the samples were annealed in the measurements reported here. They included one from each electron fluence and one control. Eight thirty-minute anneals were done starting at 250°C, and going in 100°C steps to 950°C. The furnace was brought to temperature before the sample boat was inserted. At the end of the half-hour anneal the quartz boat was pulled to the end of the quartz tube and kept in the argon atmosphere until its return to room temperature. All samples were given an RCA wash cycle before each anneal and were measured by EPR just afterwards.

The results of the electron bombardment of two samples at each of four fluences is shown in the next slide (5). The vertical axis is the ratio of the intensity after irradiation so that before for the silicon line. The horizontal line near the center is unity. The fluence is plotted on the horizontal axis. Notice the good agreement between the two samples at each fluence. The samples with the lowest fluence experienced approximately a fifty percent increase in intensity. The others all decreased in intensity, the largest change noted in the second largest fluence samples. Each point represents averages of from three to six independent measurements at room temperature.

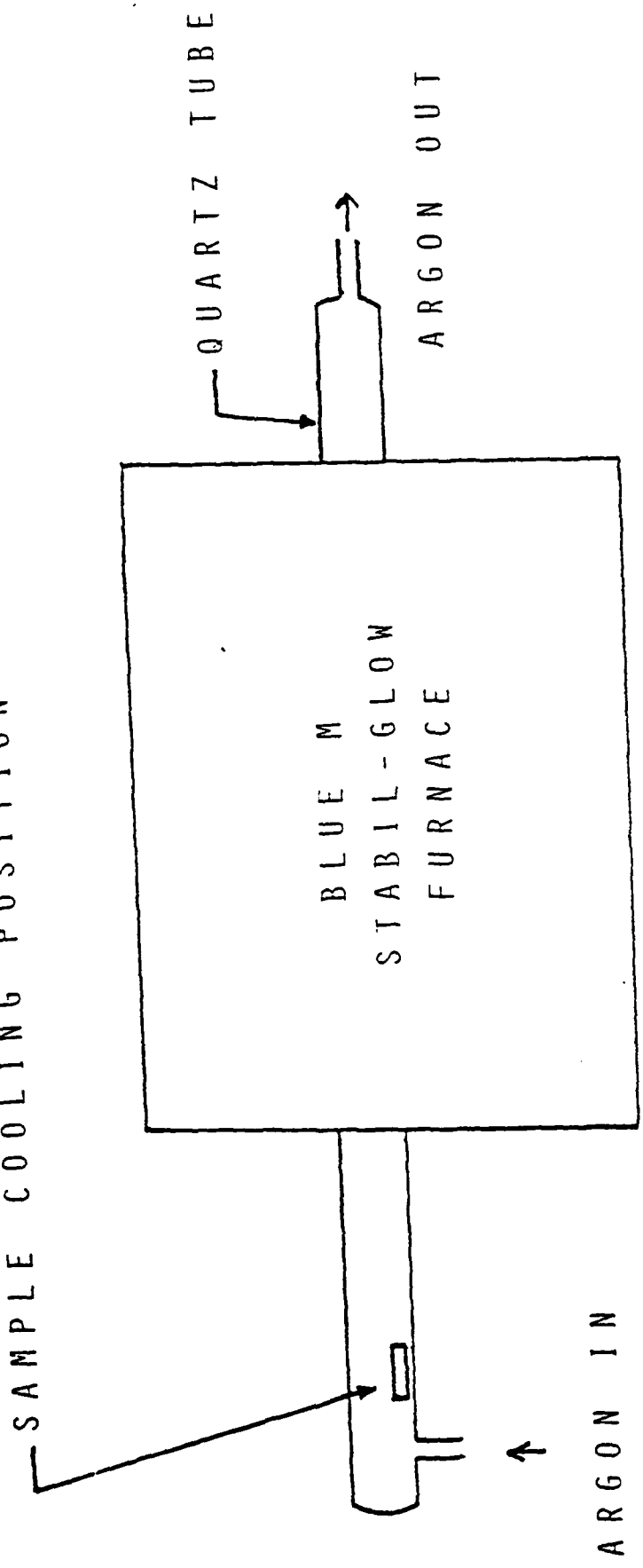
The irradiated samples were kept at 77°K until the first EPR measurements. A series of measurements were made as a function of time for several days thereafter to check for any room temperature annealing. No systematic variation was observed beyond the 17% experimental uncertainty estimated for the relative intensity measurements. The same line was examined at 77°K in several samples and the variation in intensity as a function of temperature is displayed in the next slide (6). The intensity at 77°K is about eight times that at 300°K. The variation of intensity with temperature of anneal is shown in the next slide (7) for the crystal which received the smallest fluence of 10^{16} electrons per square centimeter, and the one with largest increase in intensity during bombardment. Note that the intensity increases to 550°C and then drops abruptly above that temperature. The next slide (8) is a comparable plot for the sample with 5×10^{16} electrons per square centimeter, and the one with the largest decrease in intensity during bombardment. The shape of this curve is similar with the large peak at 550°C. The other samples, including the annealed control, exhibit this peak at 550°C, but the others grow more slowly with temperature, as for example the control in the next slide (9). It was also observed that at higher anneal temperatures the silicon line shifted to larger magnetic field values and thus lower g-values. The shift in field location is rather uniform in some samples, for example the 5×10^{16} cm^2 sample in the next slide, (12) but not in others for example the control in the next slide (11). Here one could suggest that two different lines are observed at different temperatures. The composite g-shift is similar to the control where it is difficult to establish the pattern. Of course, there would be a pattern only if the phenomenon is the same in all samples even though they had different electron fluences.

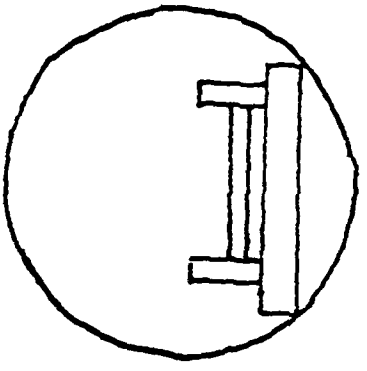
The primary defects produced by one MeV electrons in silicon are isolated vacancies and self-interstitials. However, at room temperature these defects are very mobile and are probably not significant in these measurements since the irradiations were performed at room temperature. The samples were immediately stored at 77°K until measurement, however, the lack of change in the EPR spectrum as a function of time after elevation back to 300°K confirms that these primary defects are not important. The dominant defects stable after room temperature irradiation are defect complexes which are produced when mobile primary defects are trapped by impurities and other defects. Corbett has cataloged well over one fifty such defects, most with an EPR g-value near 2. Thus unique identification is most difficult. One possibility suggested by the temperature dependence of the intensity is an aluminum-interstitial/aluminum-substitutional complex reported by Watkins. It is unique in that it is formed at about 500°C and anneals away at about 600°C, just as most of the intensity in our line, or lines, does. Additional evidence for this defect comes from the fact that the transport studies have suggested that an aluminum impurity is necessary to explain the resistivity and Hall effect data. However, additional evidence will be required to verify this tentative assignment.
This preliminary study has given us a general indication of what to expect in electron irradiated silicon. As we examine the second set of samples via anneal, we will look carefully in the neighborhood of 500°C for intensity changes, and look carefully at all temperatures for shifts in the g-value. In addition we will attempt to correlate our results with those on optical and transport properties. I would like to acknowledge the support of the National Science Foundation Undergraduate Research Participation Program. Thank you.

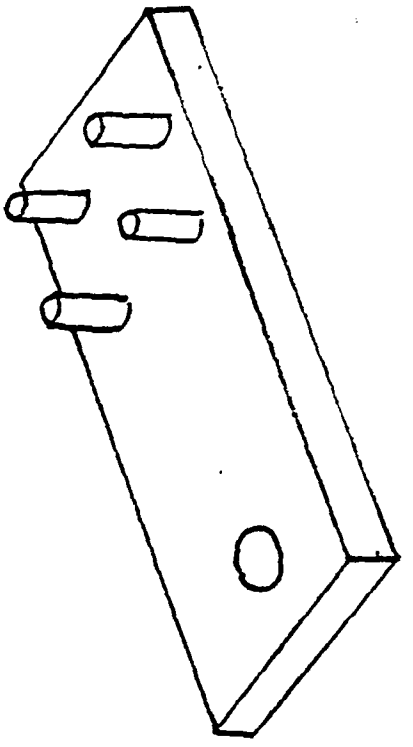
CRYSTALS	ELECTRON FLUENCE $\times 10^{16}$ E/CM^2	ANNEALED
21 22	1	YES
23 24	2	YES
25 26	5	YES
27 28	10	YES
29	NONE	YES
30	NONE	NO

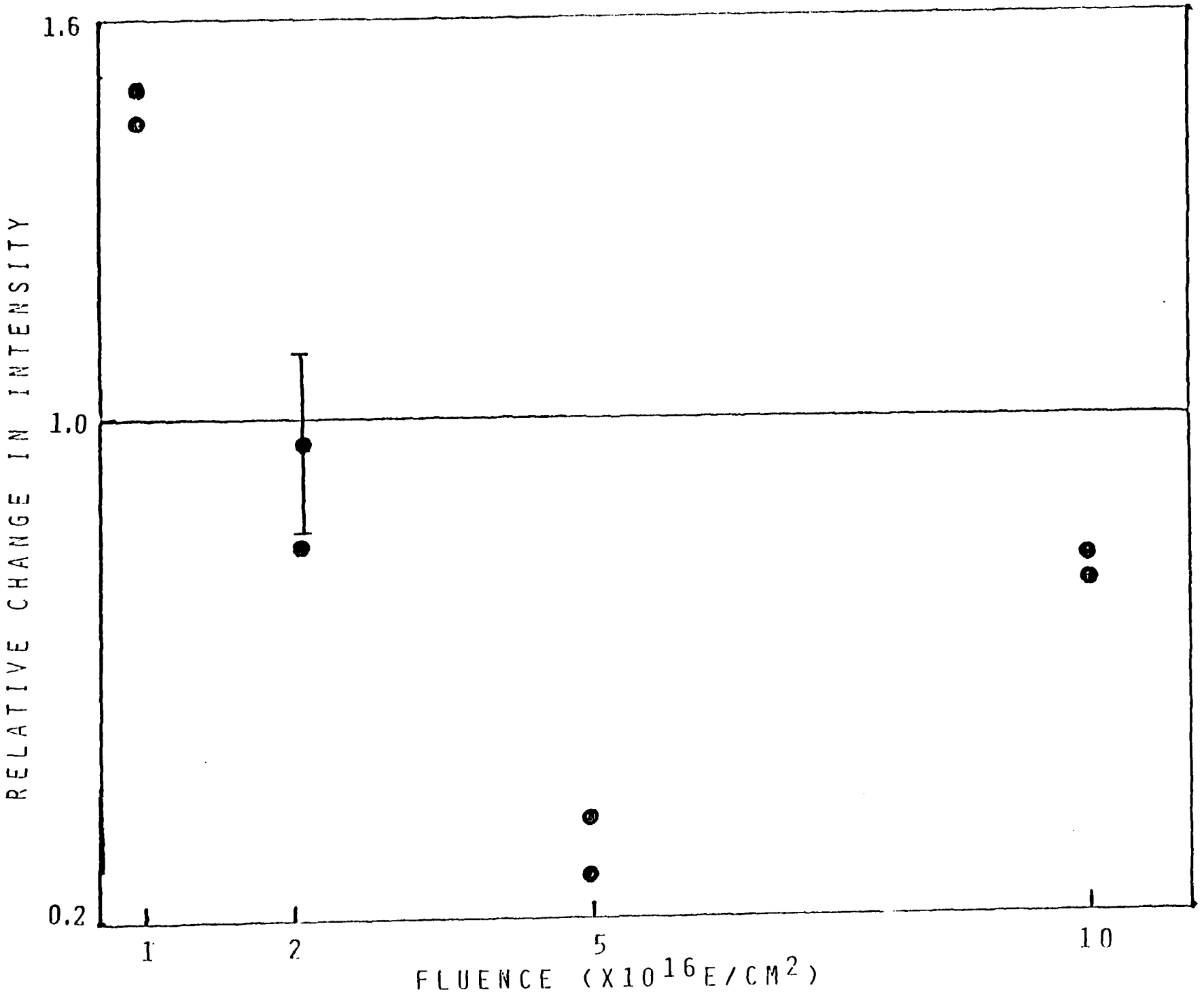

5 x 10 16 ELECTRONS / CM 2
550 °C ANNEAL
SLIDE 2

SLIDE 3

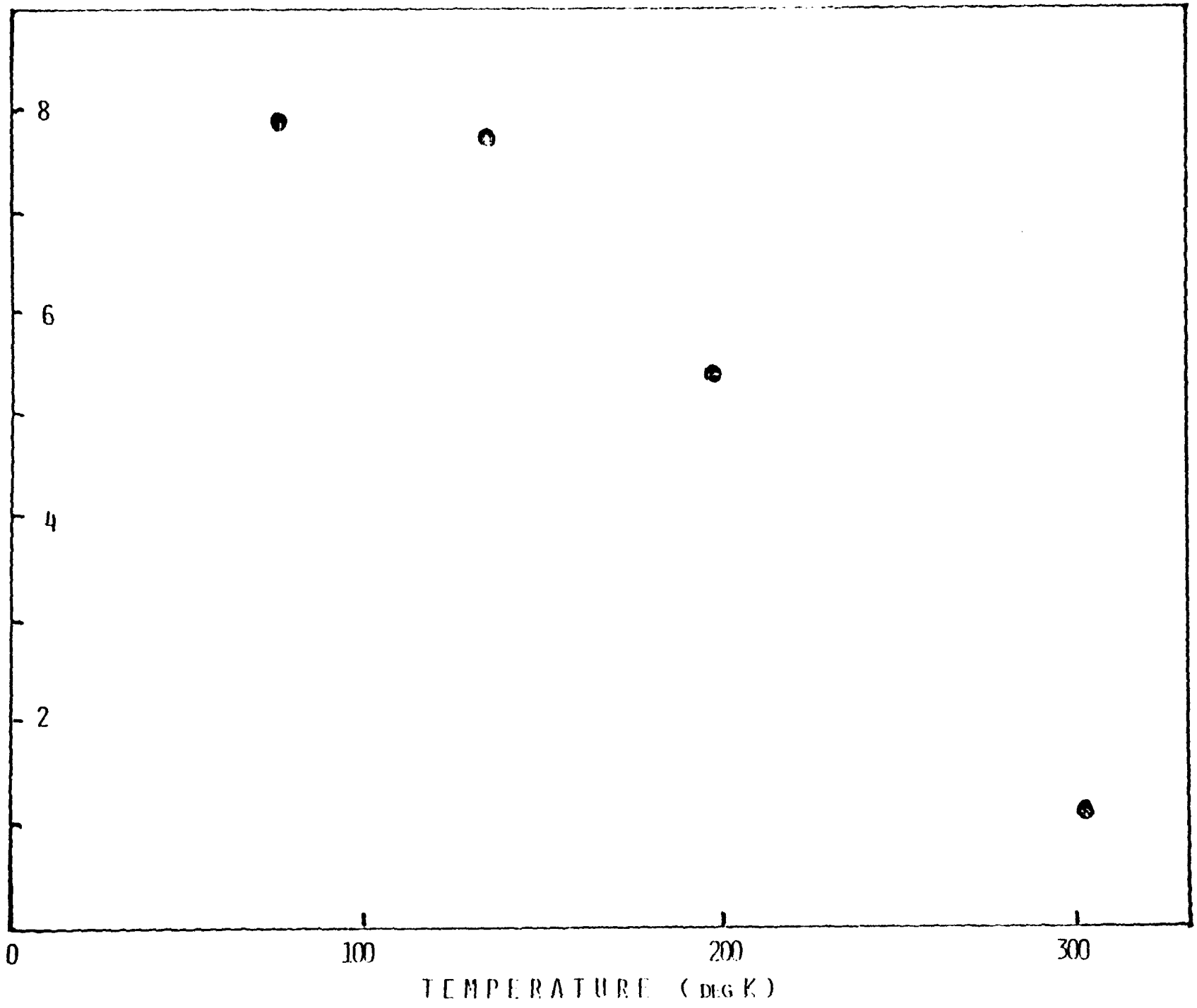

QUARTZ TUBE
ARGON OUT
BLUE M
STABIL-GLOW
FURNACE
SAMPLE COOLING POSITION
ARGON IN



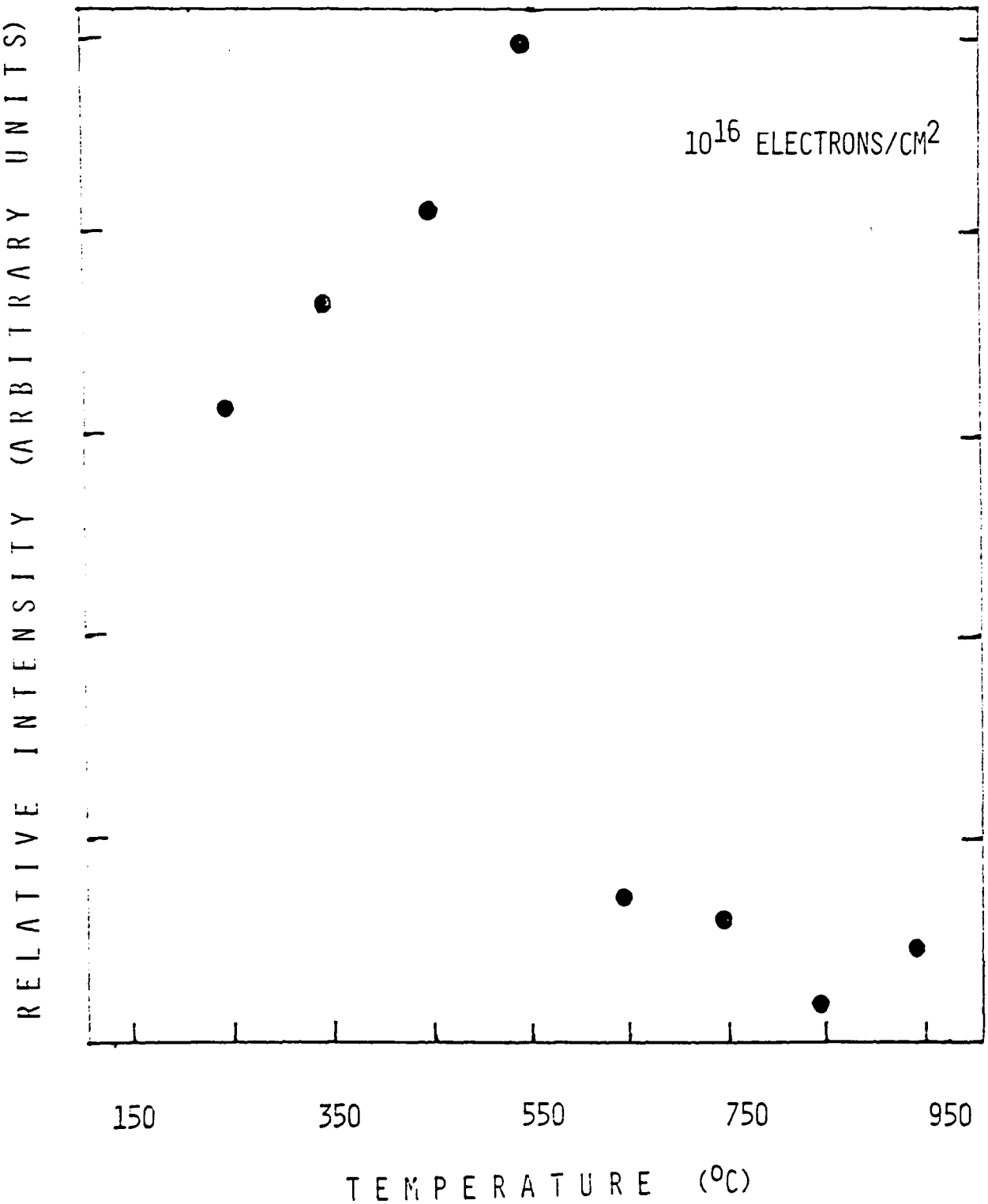


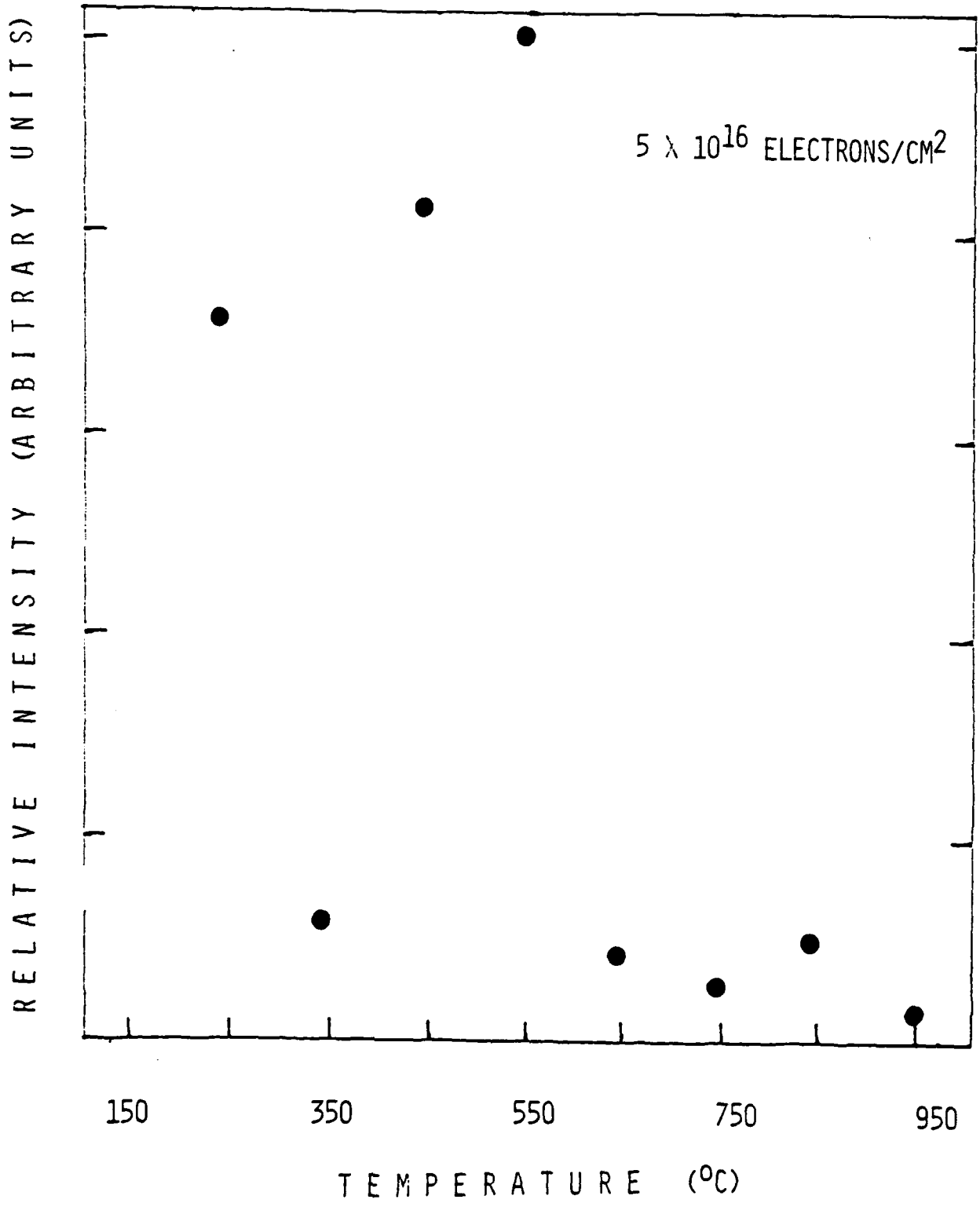

1.6
1.0
0.2
RELATIVE CHANGE IN INTENSITY
1
2
5
10
FLUENCE (X10^{16}E/CM^2)

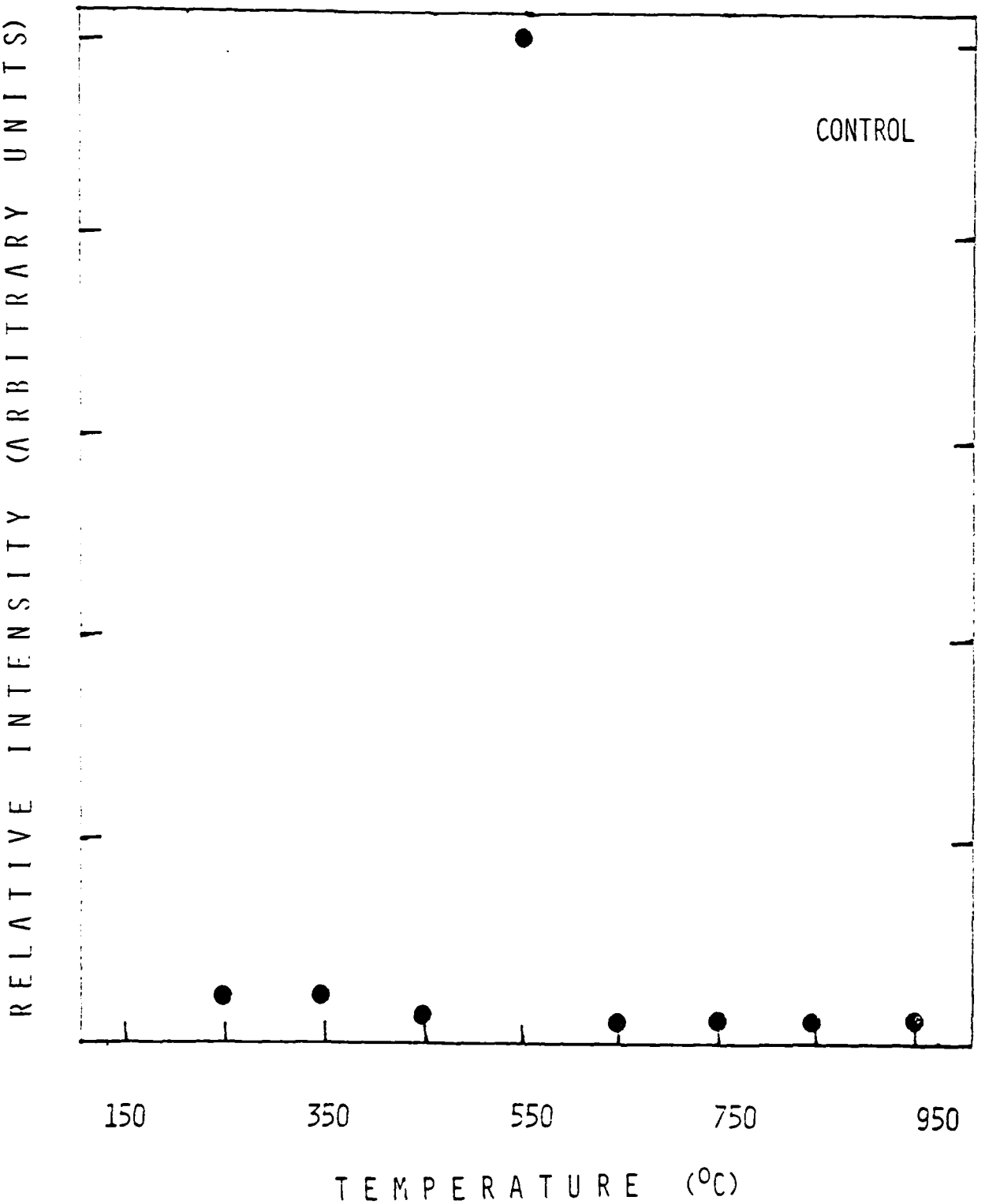
SLIDE 5

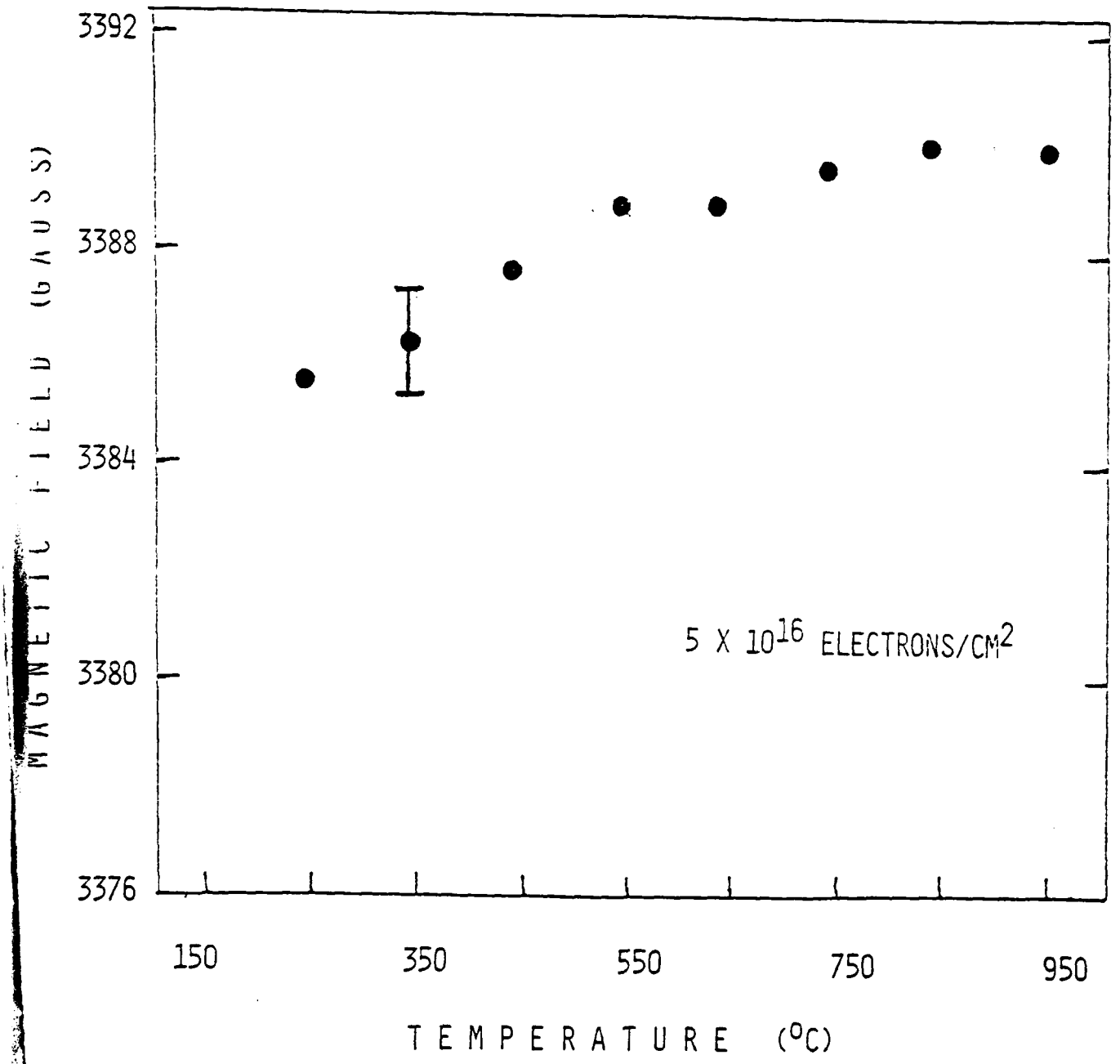

INTENSITY (RELATIVE UNITS)
8
6
4
2
0
100
200
300
TEMPERATURE (DEG K)

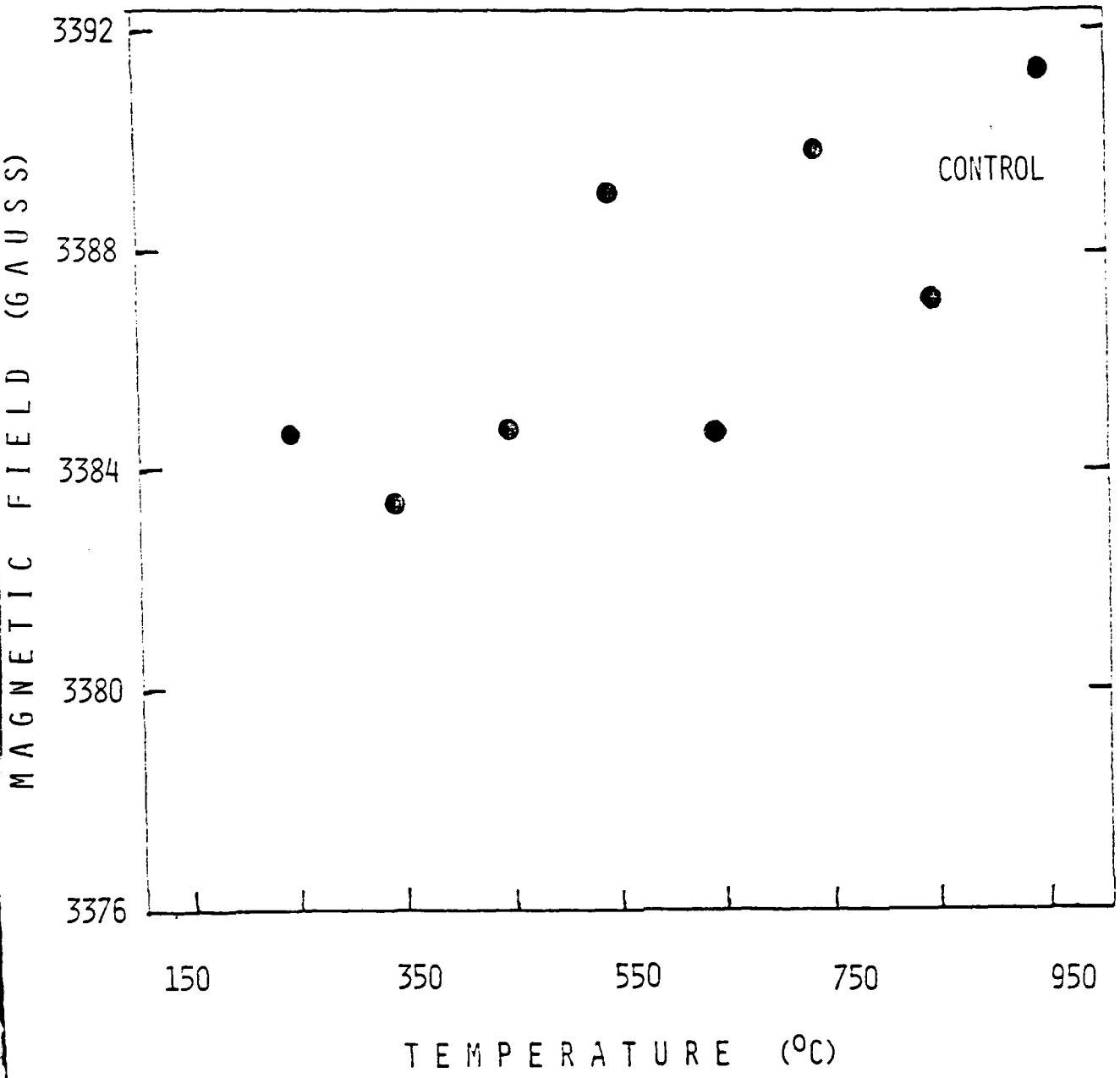
SLIDE 6


RELATIVE INTENSITY (ARBITRARY UNITS)
10^{16} ELECTRONS/CM^2
150
350
550
750
950
TEMPERATURE (°C)


RELATIVE INTENSITY (ARBITRARY UNITS)
5 λ 10^16 ELECTRONS/CM^2
150
350
550
750
950
TEMPERATURE (°C)


CONTROL
RELATIVE INTENSITY (ARBITRARY UNITS)
150
350
550
750
950
TEMPERATURE (°C)


3392
3388
3384
3380
3376
MAGNETIC FIELD (GAUSS)
5 X 10^16 ELECTRONS/CM^2
150
350
550
750
950
TEMPERATURE (°C)


3392
3388
3384
3380
3376
MAGNETIC FIELD (GAUSS)
CONTROL
150
350
550
750
950
TEMPERATURE (°C)

APPENDIX B

Abstract Submitted
for the Spring Meeting of the
American Physical Society
in Washington, DC
April 21 - 24, 1980

Reference: Bulletin of the American Physical Society 25, 548 (1980)

An Annealing Study of Indium-doped Silicon after Electron Irradiation.*GEORGE K. MINER, University of Dayton.--Indium-doped silicon has been electron irradiated in fluences ranging from 10^{16} to 10^{17} electrons per square centimeter. An electron paramagnetic resonance line near g = 2 was observed at room temperature and at 77 K. The intensity of the line was altered by the 1 MeV-electron bombardment and by subsequent annealing. These measurements will be reported and discussed in light of possible models.

*Supported in part by USAF Office of Scientific Research and USAF Materials Laboratory.

"An Annealing Study of Indium-doped Silicon after Electron bombardment."

There is much interest in the use of silicon in infrared detection. Generally it is desirable to develop detectors for the 1 to 25 micrometer range. Pure silicon is limited in its response to wavelengths of 1.1 micrometers or less. In order to extend this range, impurity atoms must be incorporated into the silicon. Some dopants of interest include indium doped silicon for response in the range 3 - 5 micrometers and gallium doped silicon for the 8 - 14 micrometer range. These extrinsic detectors may be used in a monolithic integrated circuit technology. The requirement that the detector array have a uniform ability to detect and respond from element to element dictates impurity uniformity, and the precise control of defects. Dopant concentrations range from 10^{16} to 10^{17} per cubic centimeter, and impurity concentrations are as low as 10^{12} per cubic centimeter. This requires careful materials characterization, hence the present work on indium-doped silicon.

I would like to present preliminary results of electron paramagnetic resonance (or EPR) measurements on one-MeV electron irradiated indium-doped silicon. The experiment was initiated because of reports by Swaminathan, Lang, Hemenger and Smith that the transport properties of indium-doped silicon were altered by electron irradiation. In their work they reported the observance of an unknown level, also seen by others, and generally referred to as the x-level. That group and other coworkers have now set out to perform additional measurements that include optical and transport studies. The present EPR study is coordinated with these experiments.

All the samples investigated in these experiments were cut from a single boule of Float-zone indium-doped silicon. The EPR samples were cut into wafers about one-half of a millimeter thick and had a mass in the neighborhood of 50 milligrams. A total of ten samples were studied. The treatment of the samples is shown in the first slide.(1) Two each were irradiated at each of four electron fluences ranging from 10^{16} to 10^{17} electrons per square centimeter. The remaining two samples served as controls, one of which was annealed with the irradiated samples. The irradiations were done on a 1 MeV Van de Graaff accelerator with the samples exposed from both sides of the wafer. All irradiated samples were maintained at liquid nitrogen temperature until the first EPR measurements.

The samples were oriented so that the [100]- direction was along the magnetic field. The spectrometer used was an x-band Varian Model 4500 Series. Due to the weakness of the signals at room temperature and at liquid nitrogen temperature, signal averaging was employed. Reasonable signals for most samples were collected in 25 sweeps. For the measuring of g-values and relative intensities, a manganese marker was permanently installed in the cavity. The next slide(2) shows that its location is such that the phase of its EPR line was opposite to that of the unknowns. The marker has a line approximately 50 gauss down field from the observed silicon line near g = 2 and was used for monitoring. The separation in gauss between the reference line and the sample line could be measured accurately. Also the height of the reference line was used in the measure of relative intensity.

The annealing was done in a furnace with temperature control as shown in the next slide.(3) The samples were on a quartz boat in

a quartz tube and were bathed in an argon atmosphere during heating and cooling. The samples were sandwiched between ultra-high purity silicon wafers during anneal as pictured in the next slide. Only half of the samples were annealed in the measurements reported here. They included one from each electron fluence and one control. Nine thirty-minute anneals were done starting at 250°C and going in 100°C steps to 1050°C during the first annealing cycle. During later cycles this scheme was varied. The furnace was brought to temperature before the sample boat was inserted. At the end of the half-hour anneal the quartz boat was pulled to the end of the quartz tube and kept in the argon atmosphere until its return to room temperature. All samples were given an RCA wash cycle before each anneal and were measured by EPR just afterwards.

The results of the electron bombardment of two samples at each of four fluences is shown in the next slide. The vertical axis is the ratio of the silicon line intensity after irradiation to the intensity before irradiation. The horizontal line near the center is unity. The fluence is plotted on the horizontal axis. Notice the good agreement between the two samples at each fluence. The samples with the lowest fluence experienced approximately a fifty percent increase in intensity. The others all decreased in intensity, the largest change noted in the second largest fluence samples. Each point represents an average of from three to six independent measurements at room temperature. The irradiated samples were kept at 77°K until the first EPR measurements. A series of measurements were made as a function of time for several days thereafter to check for any room temperature annealing. No systematic variation was observed beyond the 17% experimental uncertainty estimated for the

relative intensity measurements. The same line was examined at 77°K in several samples and the variation in intensity as a function of temperature is displayed in the next slide. The intensity at 77°K is about eight times that at 300°K. The variation of intensity with temperature of anneal is shown in the next slide for the crystal which received the smallest fluence of 10^{16} electrons per square centimeter, the one with largest increase in intensity during bombardment. Note that the intensity increases to 550°C and then drops abruptly above that temperature. The next slide is comparable plot for the sample with 5×10^{16} electrons per square centimeter, and the one with the largest decrease in intensity during bombardment. The shape of this curve is similar with the large peak at 550°C. The other samples, including the annealed control, exhibit this peak at 550°C, but the others grow more slowly with temperature, as for example the control in the next slide.

Due to the observed increase and decrease in this line as anneal temperature is increased, a second anneal cycle was run on each crystal. For the 10^{16} per-square-cm sample, both anneal cycles are shown in the next slide. Relative intensity is plotted on the vertical and anneal temperature on the horizontal, and repeated for the second cycle. Note that the peak near 500°C is five-times more intense on the second cycle. The same observation is made in the 2-times-10^{16} per-square-cm sample. The sample with 5×10^{16} electrons per square cm is shown in the next slide where the second cycle peak is larger only by a factor of 3. In the 10^{17} per-square-cm sample the factor is about one.

The control shown in the next slide shows a much reduced peak in the second cycle, but a partial recovery in a third cycle.

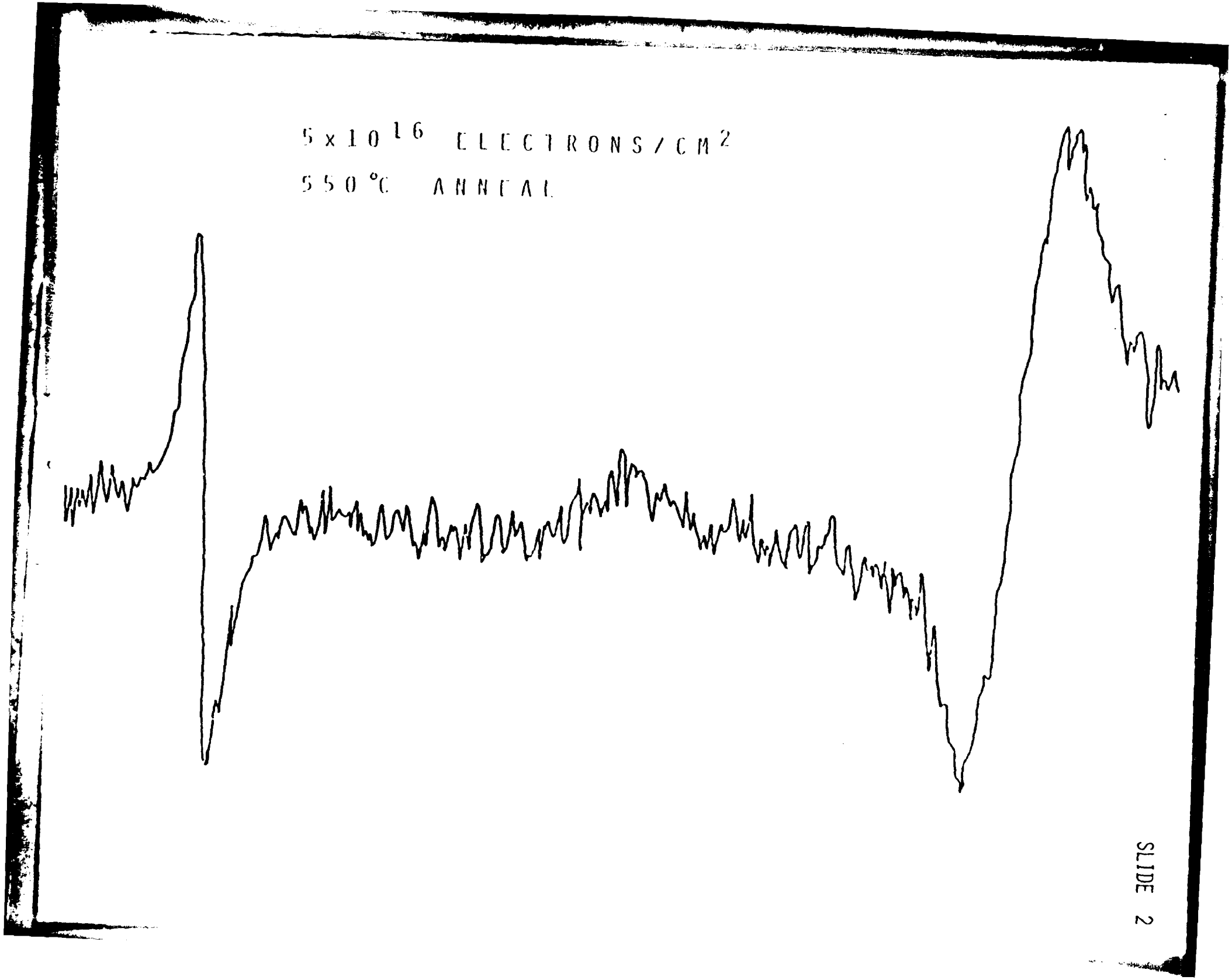
For comparison several other samples, both indium-doped and relatively pure, were examined. They are identified in the next slide. The first two are from two other boules and the last three from a single boule. The next slide shows an anneal cycle for each of the indium-doped-but-not-electron-irradiated samples. They both show the line and the growth of its intensity near 500°C. One of the undoped samples was taken through the anneal cycle and the results are given in the next slide. The results are similar to the other samples. However the other two undoped samples were taken directly to 550°C for a 30-minute anneal. In each of these two samples the line had disappeared after this anneal.

It was also observed that at higher anneal temperatures the silicon line shifted to larger magnetic field values and thus lower g-values. The shift in field location is rather uniform in some samples, for example the 5 x 10^{16} cm^2 sample in the next slide, but not in others, for example the control in the next slide. There one could suggest that two different lines are observed at different temperatures.

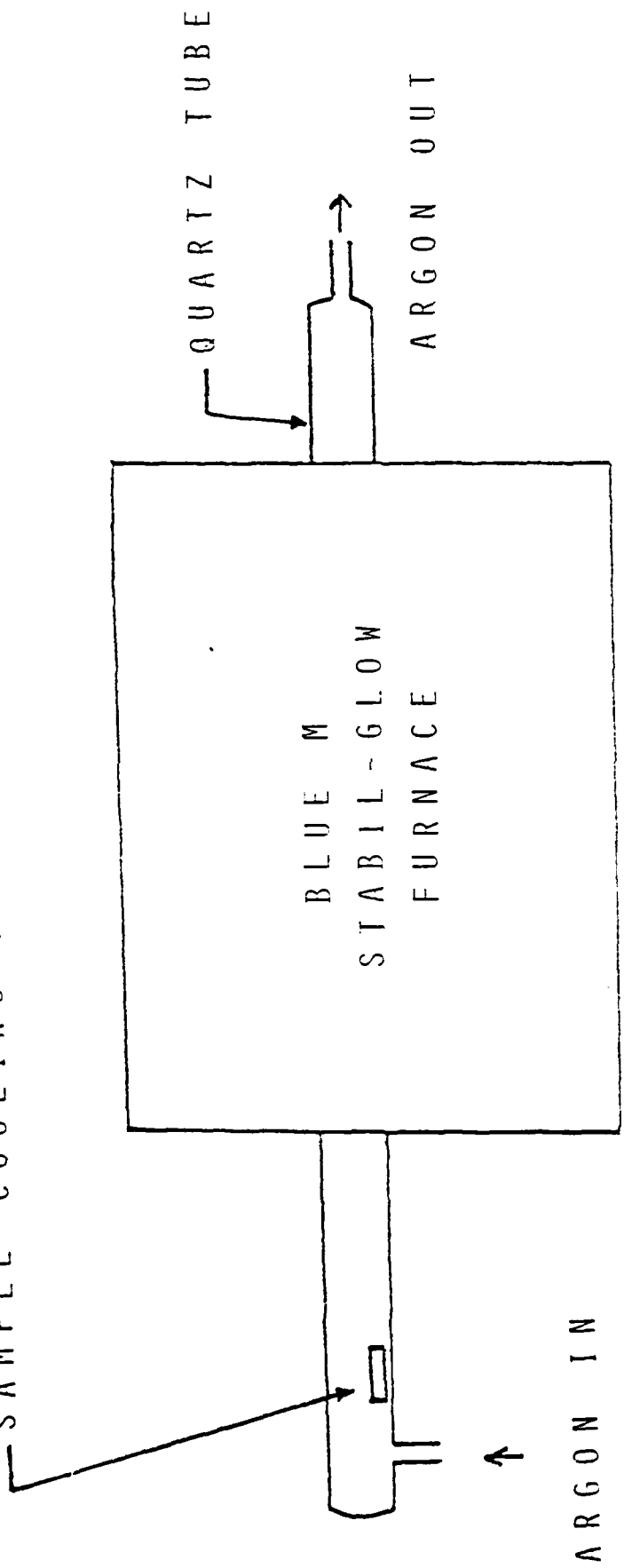
The primary defects produced by one MeV electrons in silicon are isolated vacancies and self-interstitials. However, at room temperature these defects are very mobile and are probably not significant in these measurements since the irradiations were performed at room temperature. The samples were immediately stored at 77°K until measurement, however, the lack of change in the EPR spectrum as a function of time after elevation back to 300°K confirms that these primary defects are not important. The dominant defects stable after room temperature irradiation are defect

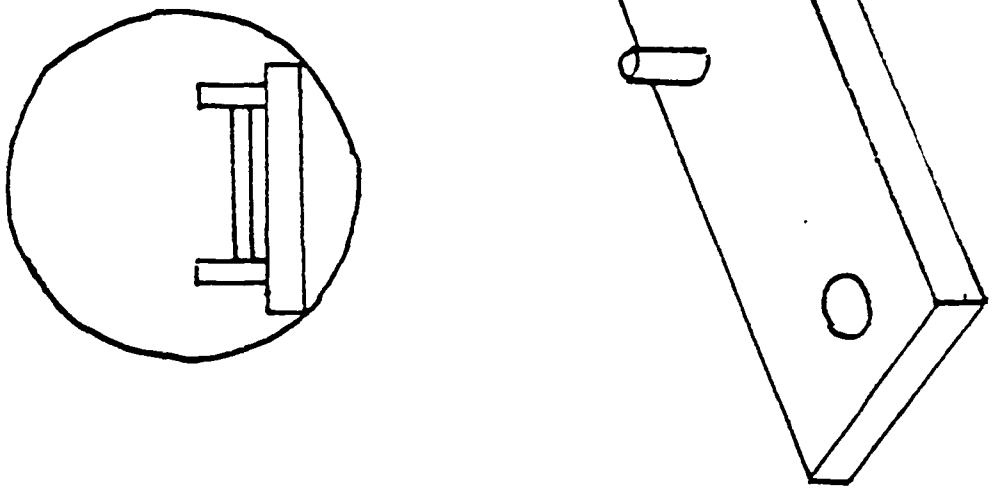
complexes which are produced when mobile primary defects are trapped by impurities and other defects. Corbett has cataloged well over some fifty such defects, most with an EPR g-value near 2. Thus unique identification is most difficult. One possibility suggested by the temperature dependence of the intensity is an aluminum-interstitial/aluminum-substitutional complex reported by Watkins. It is unique in that it is formed at about 500°C and anneals away at about 600°C, just as most of the intensity in our line, or lines, does. Additional evidence for this defect comes from the fact that the transport studies have suggested that an aluminum impurity is necessary to explain the resistivity and Hall effect data. Another possibility is the so-called P1-center-a pentavacancy cluster. It grows above ~170°C following liberation of vacancies from P3-centers. The P1-center anneals near 500 - 600°C, consistent with the data. This preliminary study has given us a general indication of what to expect in electron irradiated silicon. As we examine the second set of samples via anneal, we will look carefully in the neighborhood of 500°C for intensity changes, and at all temperatures for shifts in the g-value. In addition we will attempt to correlate our results with those of the optical and transport properties. Thank you.

CRYSTALS	ELECTRON FLUENCE $\times 10^{16}$ E/CM^2	ANNEALED
21 22	1	YES
23 24	2	YES
25 26	5	YES
27 28	10	YES
29	NONE	YES
30	NONE	NO

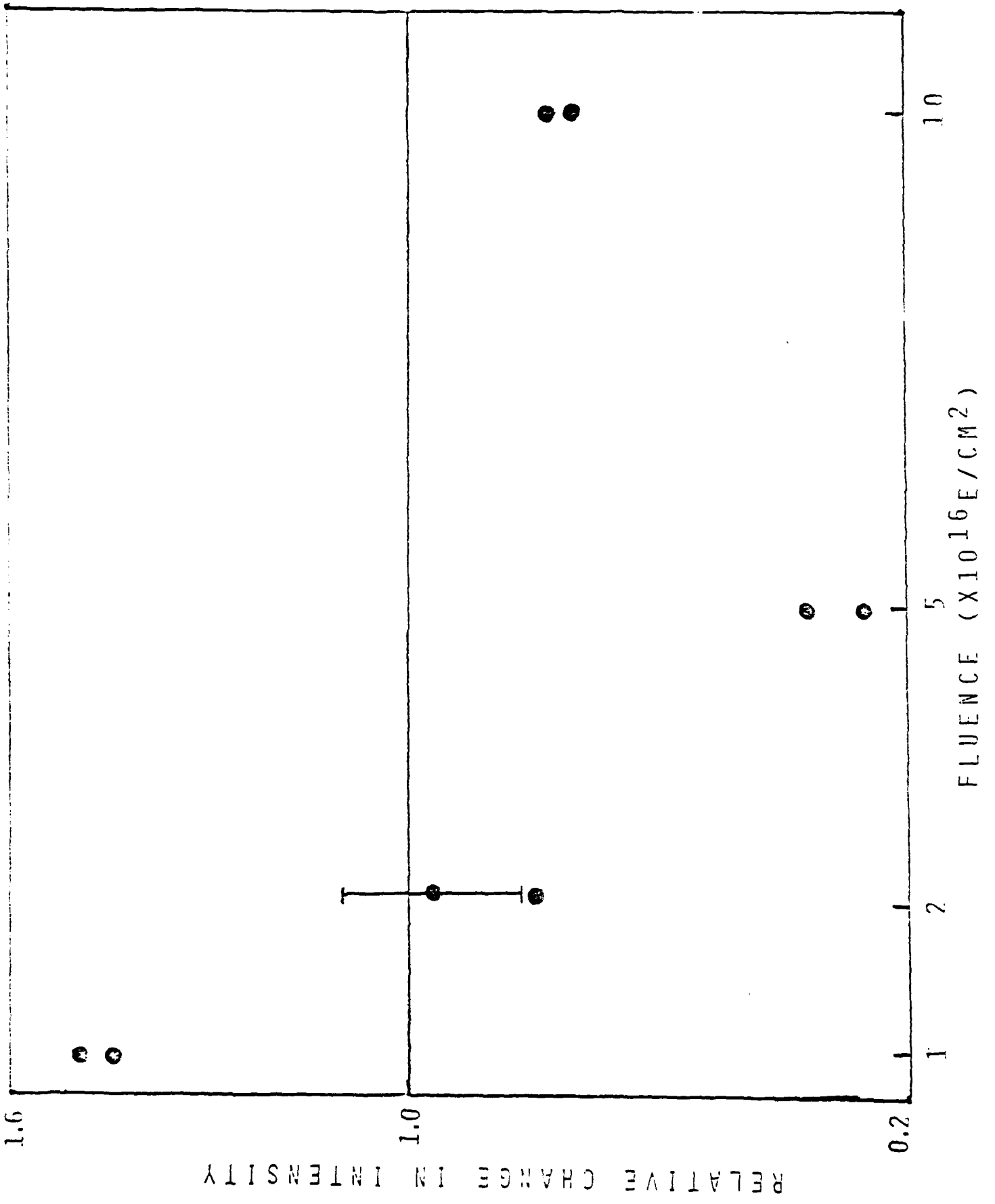

5 x 10 16 ELECTRONS / CM 2
550 °C ANNEAL
SLIDE 2

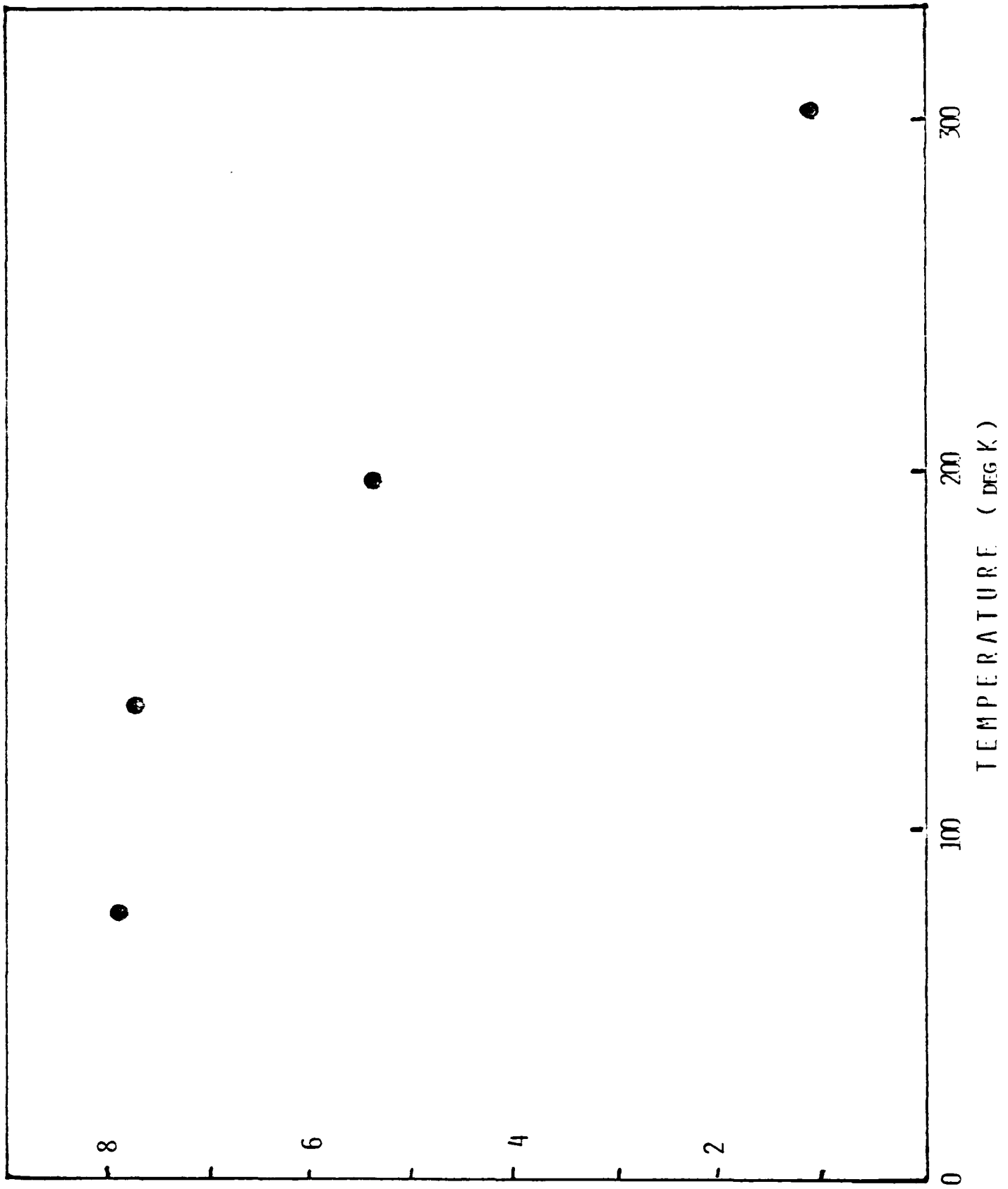
SLIDE 3


QUARTZ TUBE
ARGON OUT
BLUE M
STABIL-GLOW
FURNACE
SAMPLE COOLING POSITION
ARGON IN

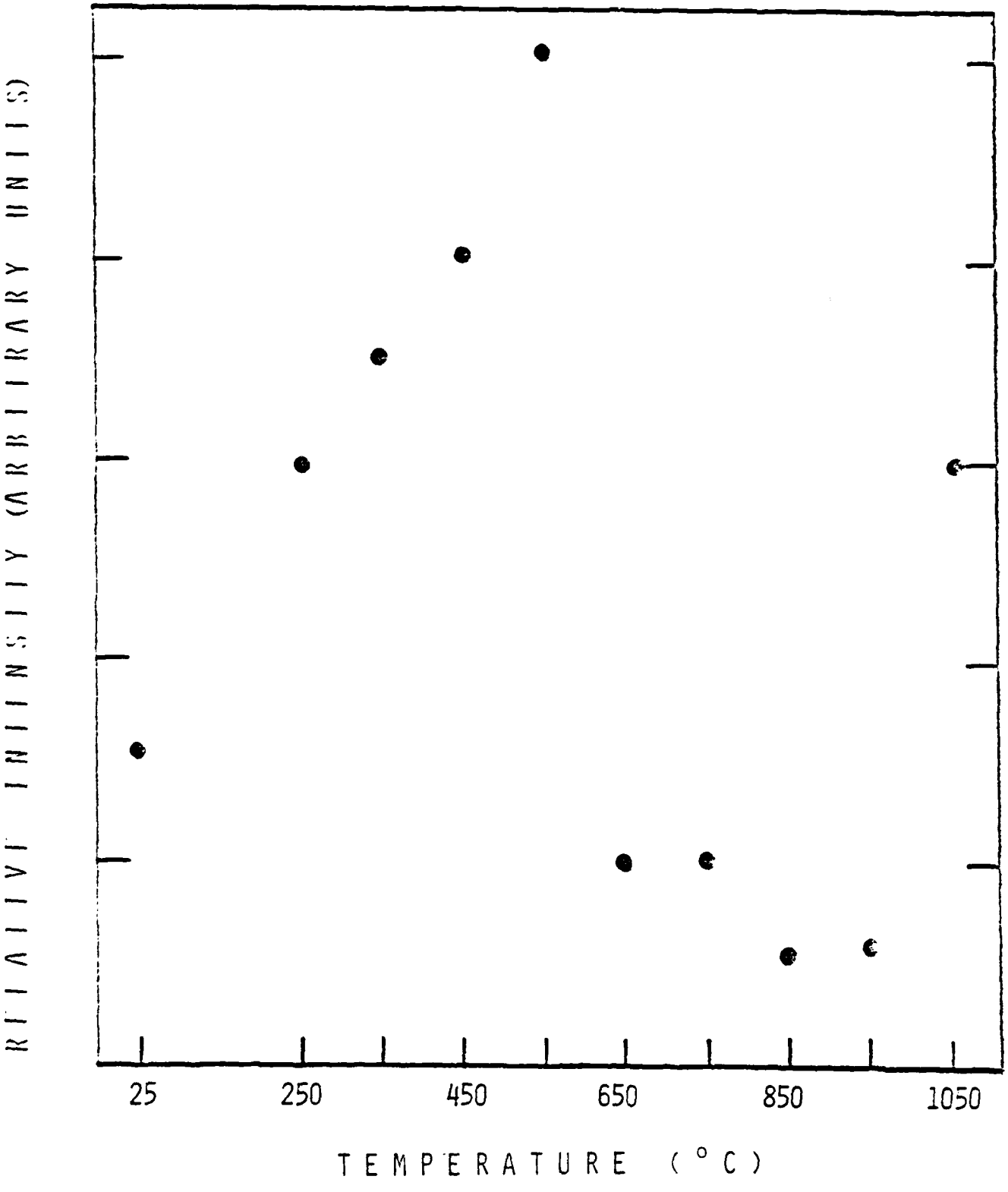


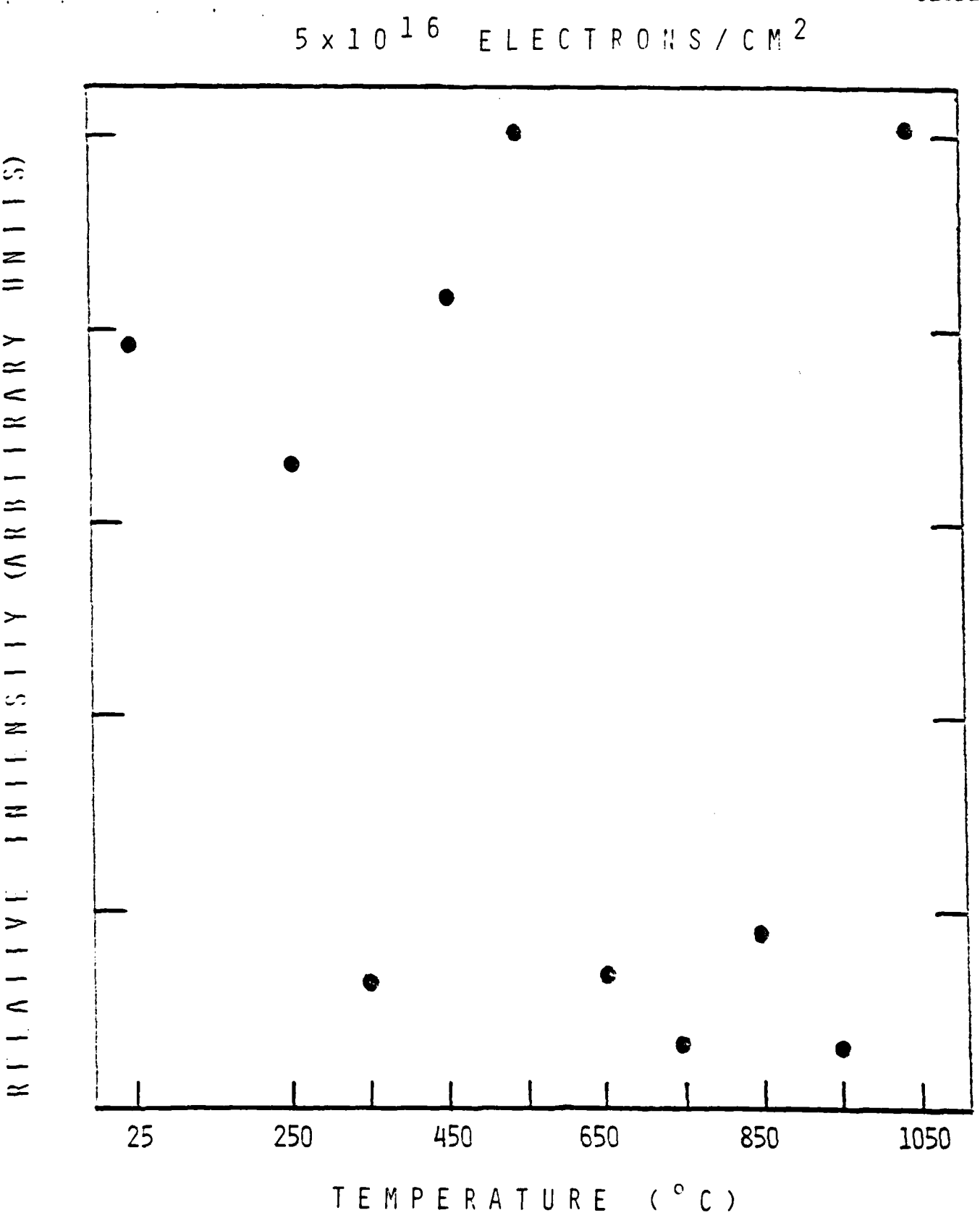
SLIDE 5


RELATIVE CHANGE IN INTENSITY
1.6
1.0
0.2
1
2
5
10
FLUENCE (X10^{16}E/CM^2)

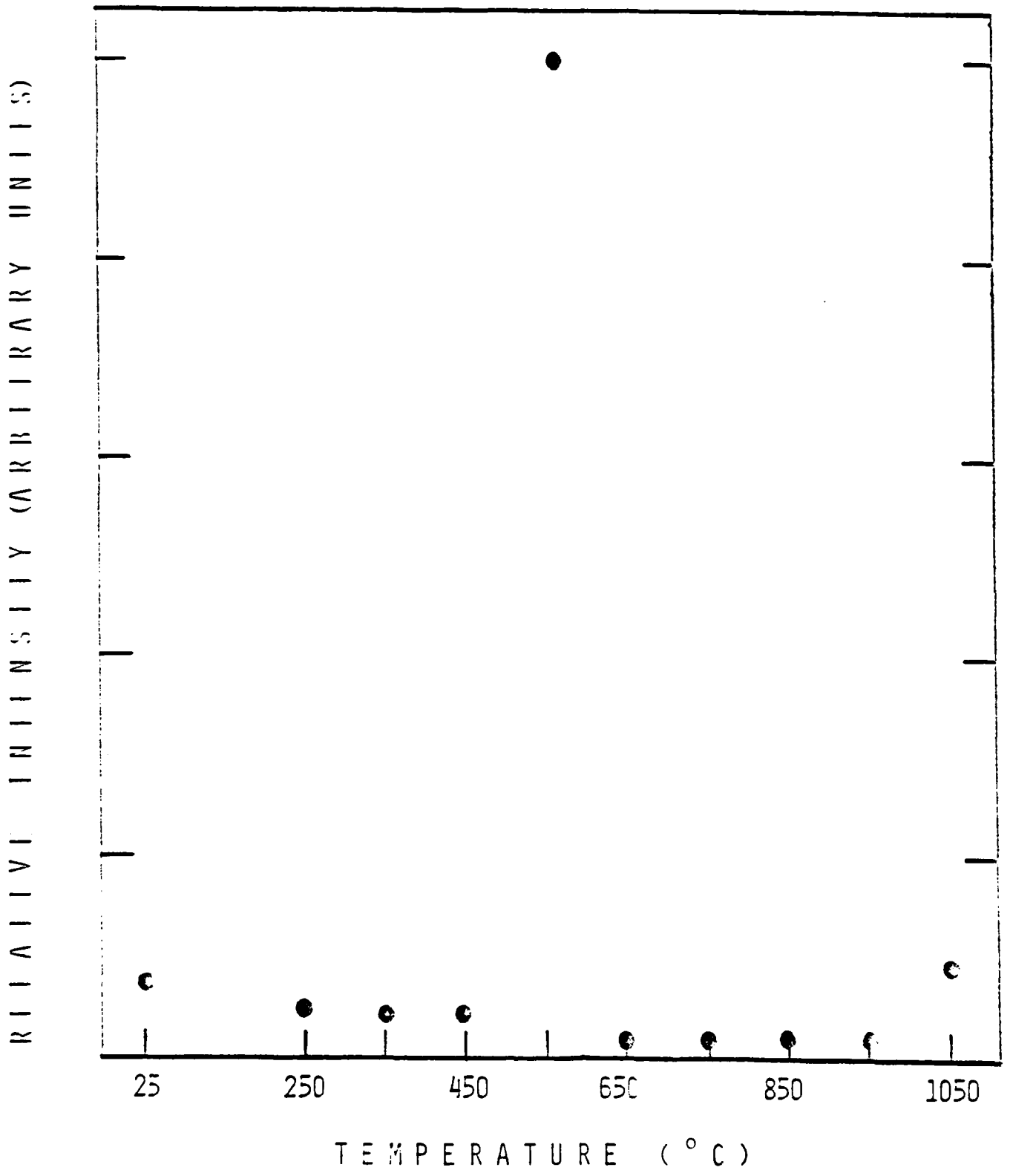

INTENSITY (RELATIVE UNITS)
0
2
4
6
8
100
200
300
TEMPERATURE (DEG K)

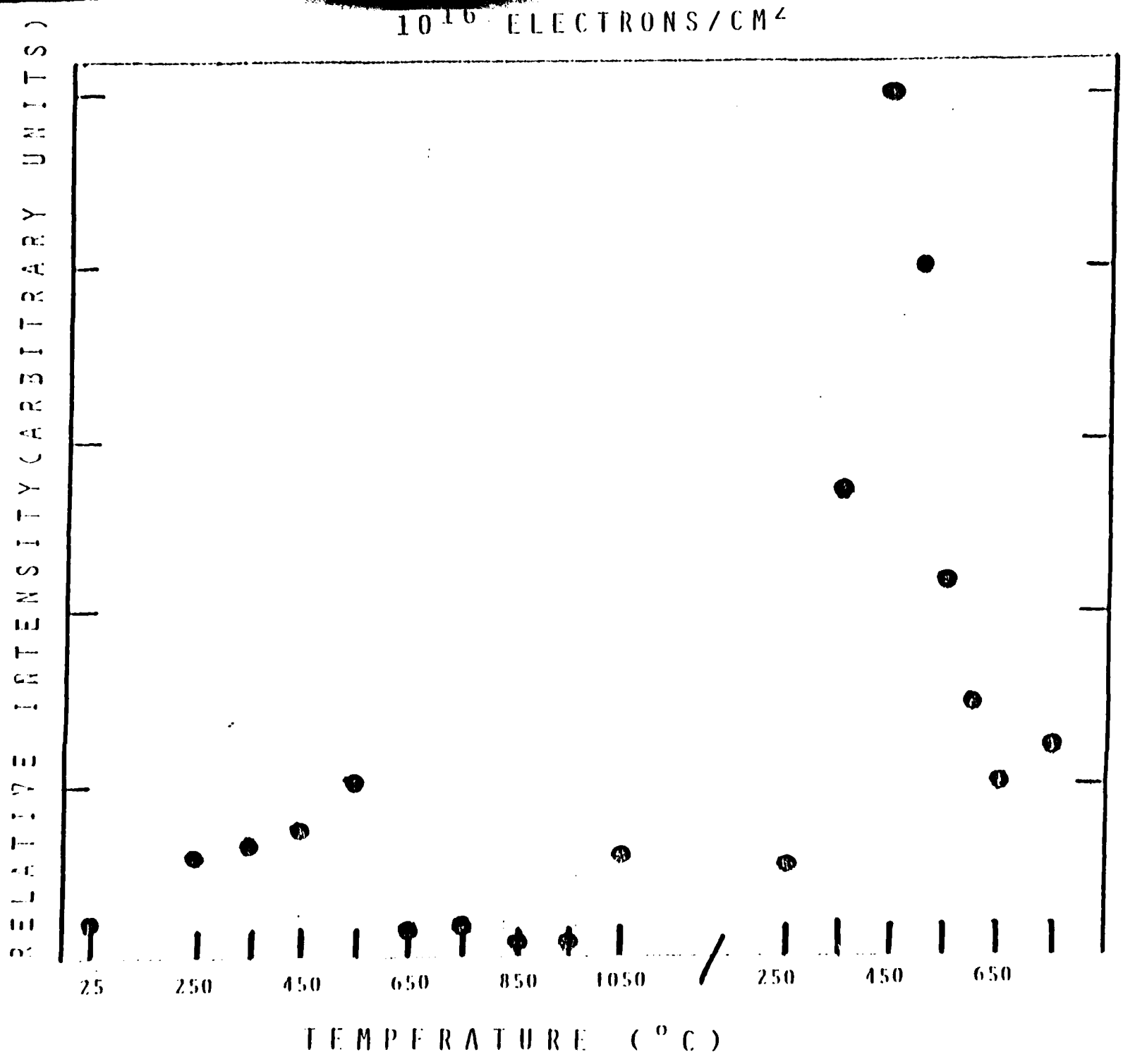
10^{16} ELECTRONS/CM^2



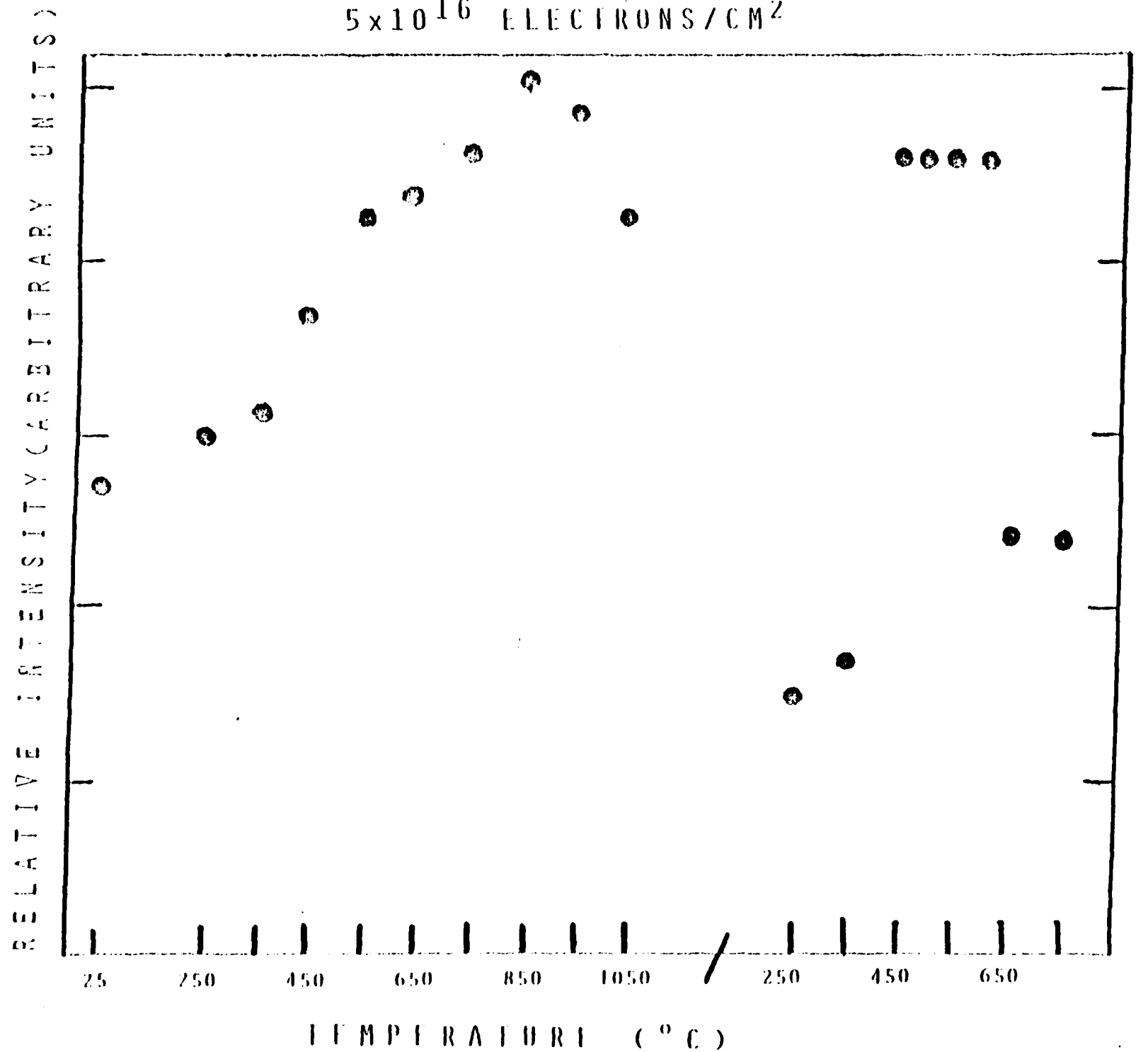

5 x 10 16 ELECTRONS / CM 2
RELATIVE INTENSITY (ARBITRARY UNITS)
25
250
450
650
850
1050
TEMPERATURE (°C)

CONTROL


RELATIVE INTENSITY (ARBITRARY UNITS)
25
250
450
650
850
1050
TEMPERATURE (°C)


10^{16} ELECTRONS/CM^2
SELENIDE LUMINESCENCE INTENSITY (ARBITRARY UNITS)
25
250
450
650
850
1050
250
450
650
TEMPERATURE (°C)

SLIDE 10

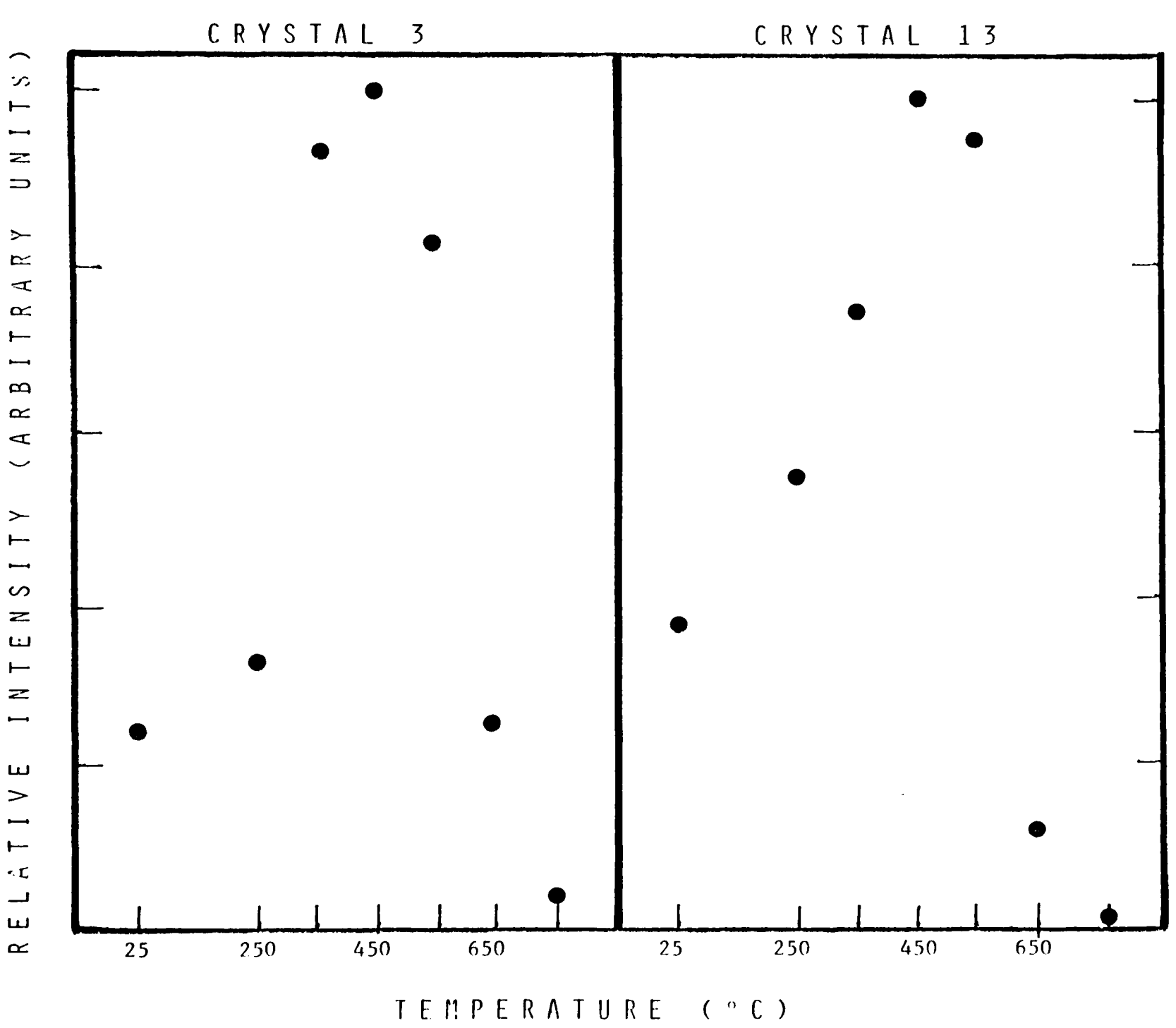

5x10^16 ELECTRONS/CM^2
RELATIVE IRRADIATION INTENSITY (ARBITRARY UNITS)
25
250
450
650
850
1050
250
450
650
TEMPERATURE (°C)

SLIDE 11

SLIDE 12

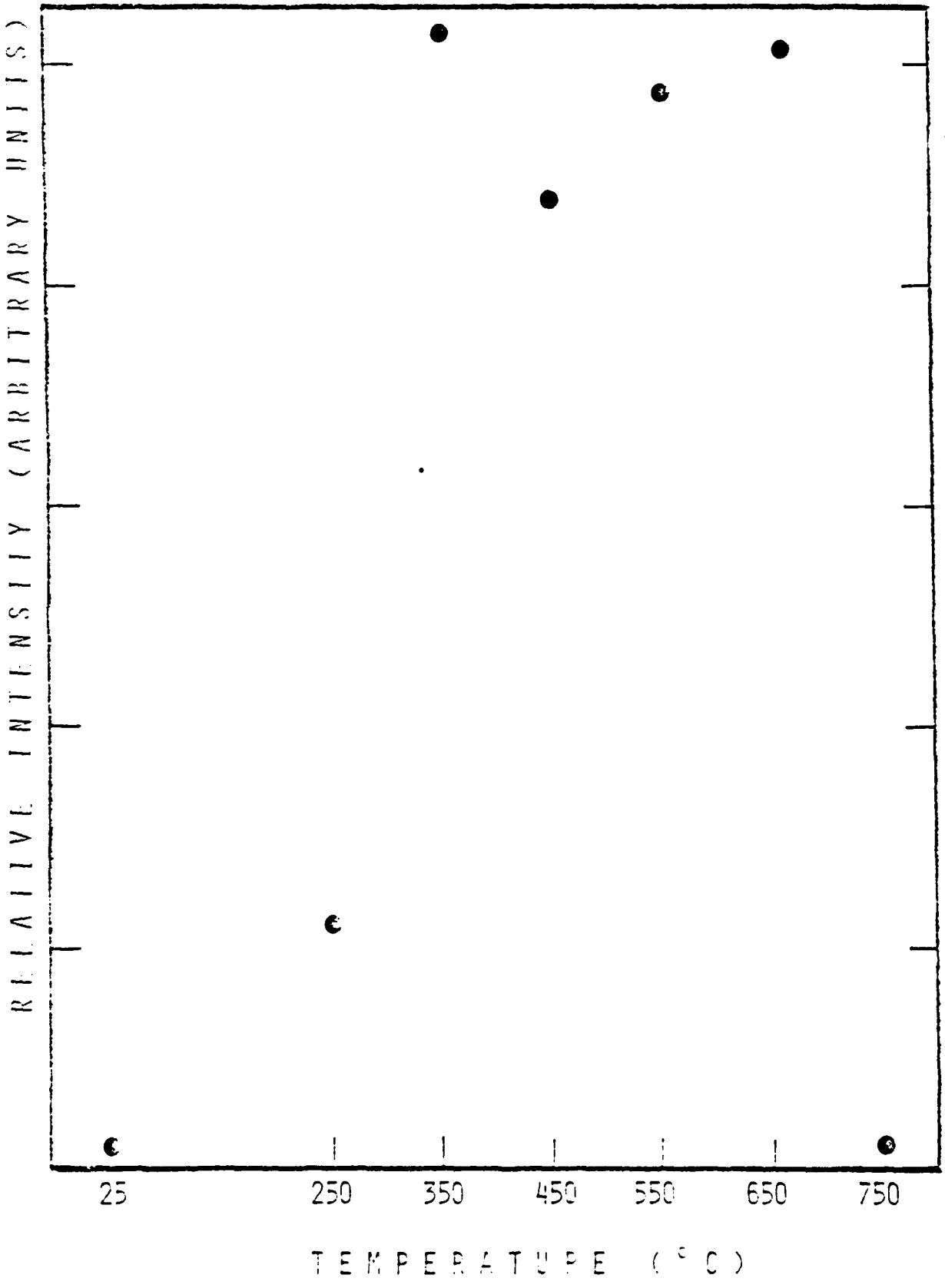
RELATIVE INTENSITY (ARBITRARY UNITS)
25
250
550
850
1050
250
550
750
250
550
750
TEMPERATURE (°C)

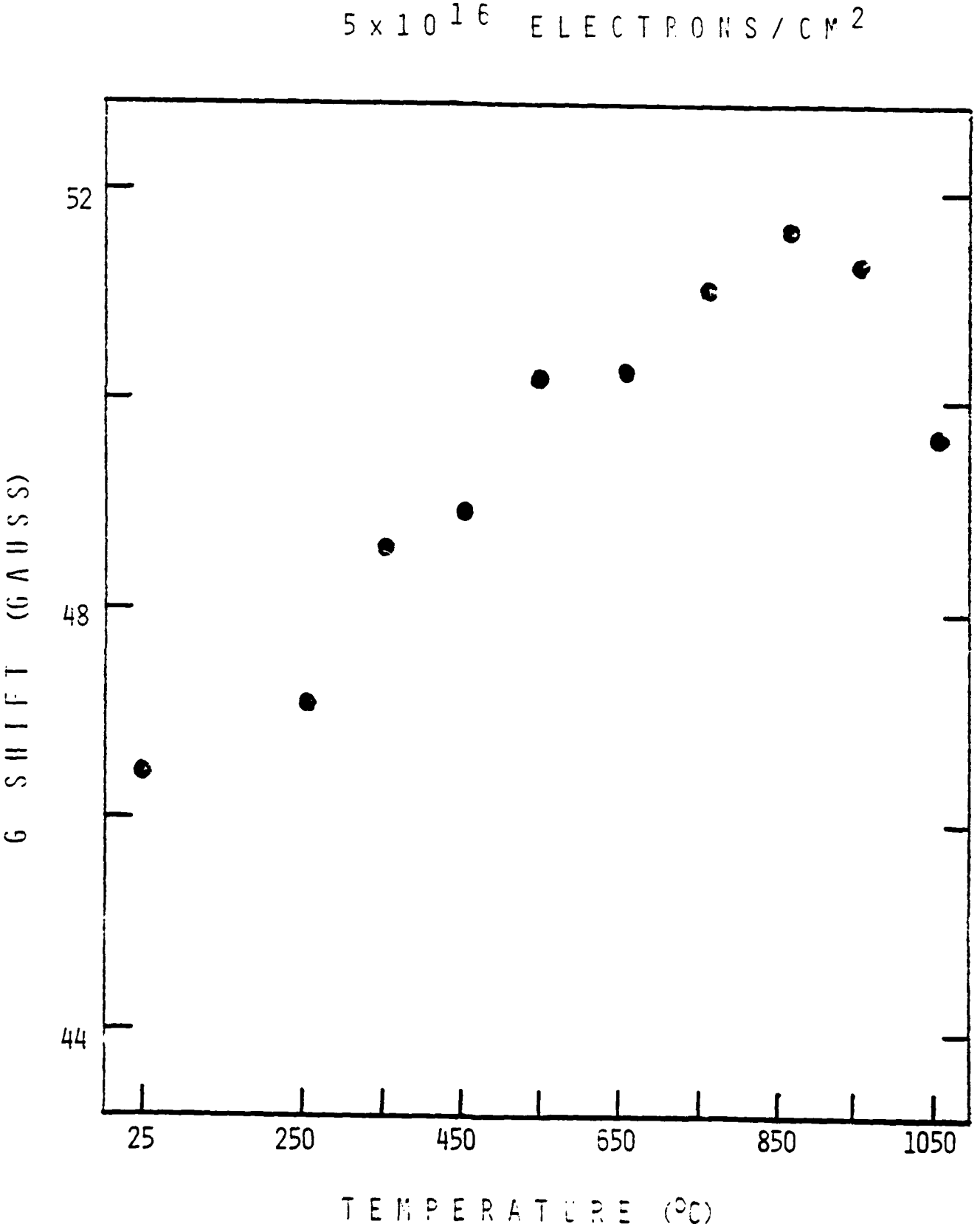
CRYSTAL	IDENTIFICATION
3	INDIUM DOPED
13	INDIUM DOPED
18	UNDOPED
19	UNDOPED
40	UNDOPED


CRYSTAL 3
CRYSTAL 13
RELATIVE INTENSITY (ARBITRARY UNITS)
25
250
450
650
25
250
450
650
TEMPERATURE (°C)

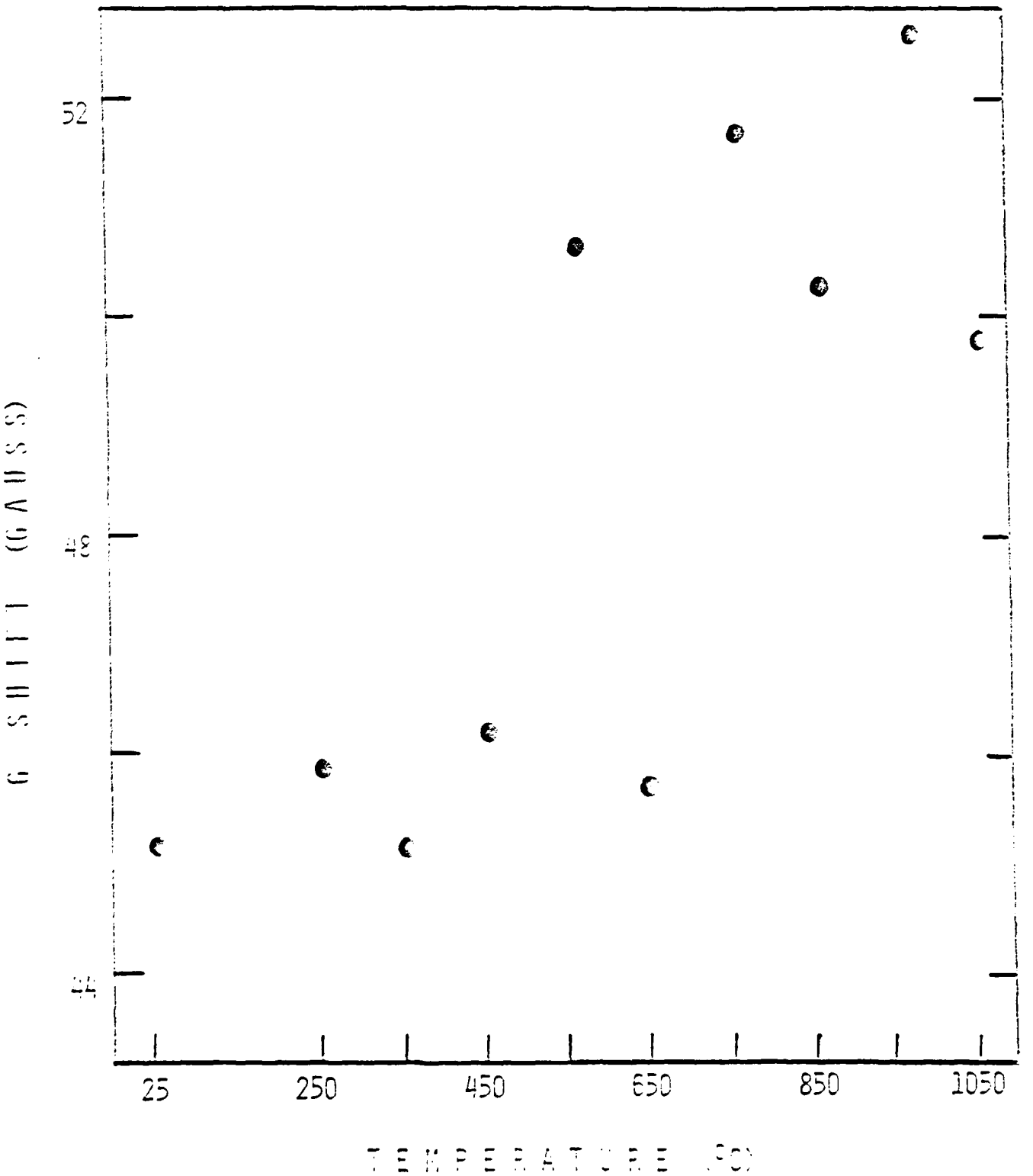
SLIDE 14

CRYSTAL 19


RELATIVE INTENSITY (ARBITRARY UNITS)
25
250
350
450
550
650
750
TEMPERATURE (°C)


5 x 10 16 ELECTRONS / CM 2
52
48
44
G SHIFT (GAUSS)
25
250
450
650
850
1050
TEMPERATURE (°C)

CONTROL



APPENDIX C

Abstract Submitted

for the Spring Meeting of the

Ohio Section of the American

Physical Society

May 9 - 10, 1980

Reference: Bulletin of the American Physical Society 25, (1980)

EPR Measurements in Silicon Doped with Boron, Gallium, or Indium Acceptors.* JOHN N. MEDER† AND GEORGE K. MINER, Univ. of Dayton.--We report electron paramagnetic resonance measurements on silicon doped with several acceptors. They include boron, gallium, and indium, with the boron introduced both during float-zoning and by implantation. A line near g = 2 was observed in each sample at room temperature and at liquid nitrogen temperature. The effects of various heat treatments will be described and discussed.

*Supported in part by USAF Office of Scientific Research and USAF Materials Laboratory.

†NSF Undergraduate Research Participant.

"EPR Measurements in Silicon Doped with Boron, Gallium, or Indium Acceptors"

First Slide (1). Silicon materials are used in a wide range of applications. Included are uses as different as infrared detection and solar collection. Since pure silicon material is limited in its response to wavelengths of 1.1 micrometer or less, impurity atoms are normally introduced to extend the range. For example, indium provides response in the 3-5 micrometer range and gallium provides response in the 8-14 micrometer range. For use in detector arrays, uniform detection ability is needed and thus careful study of these materials is needed. We would like to report preliminary electron paramagnetic resonance or (EPR) measurements at room temperature on silicon prepared in four different ways with acceptor dopants. These will be compared with an undoped material and a donor doped material. A survey of the materials studied is given in the next slide. (2)

All samples were oriented so that the [100]-direction was parallel to the magnetic field. The spectrometer used was an x-band Varian Model 4500 series. As the signals at room temperature were weak, signal averaging was employed. All traces made were the result of 25 sweeps.

For measuring the g-values and the relative intensities of the sample, a permanent manganese marker was installed in the cavity such that the phase of the signal from it was inverted to that of the sample. Manganese has a six line hyperfine spectrum, the third and fourth of which appear in the next slide (3). The separation of these two lines is 86.9 ± 0.2 gauss. The observed line of each sample was found 44 to 52 gauss up field

from the third manganese line, near g = 2, and the exact location of a particular line was also used as a reference in intensity calculations.

The annealing treatments were done in a Blue M Stable Glow Furnace with temperature control, as shown in the next slide (4). The samples were sandwiched between high purity silicon wafers and placed on a quartz boat. The boat rested in a quartz tube, through which a slight overpressure of argon gas flowed. Temperature was monitored with a thermocouple placed by the boat. The quartz tube extended beyond the furnace and had an opening at one end so that the boat could be pulled out of the furnace to cool quickly in the argon atmosphere

Samples with all six different dopants were annealed in 100° steps from 250° to 750°C. All anneals lasted one-half hour. Anneals up to 1050°C in 100°C increments, 250°C to 750°C in a second cycle and a third cycle were done on the indium doped material.

In this slide (5), the g-value for the observed sample line for room temperature measurements is given for each of the samples. Note the extreme similarity of the g-value for the four acceptor dopants, crystals 1-4. No line was observed in the undoped crystal at room temperature. The g-value for the donor was significantly lower. This slide (6) shows the relative intensity, per unit mass, of the six samples. Note that the donor sample (Phosphorous) was considerably higher in intensity than the four acceptor doped samples.

The following series of overheads shows the intensity results of annealing studies on each of the six dopants. On the vertical axis is the relative intensity, scaled to be maximum intensity observed for that sample. This overhead (7) shows the annealing studies

results for both boron doped samples, the boron-implanted data shown in triangles. Note the close correspondence of the two sets of data. Also shown is a sample error range, at about 17%. A similar plot for the gallium doped sample is shown in this slide (8). The pattern is opposite of the boron, increasing up to 350°C and decreasing thereafter.

This slide (9) shows annealing treatments on indium doped silicon, which as mentioned earlier, were much more extensive. The annealing temperatures are plotted in the order in which they were done, that is the first cycle, separated by the slash, then the second cycle, separated by a slash, then the third. Note that the intensity in the line at 550°C in the first cycle is not observed in the second cycle, and than that intermediate intensities are observed at all temperatures in the third.

This slide (10) shows a similar plot for the undoped sample. Note that a line was observed after annealing at 250°C, and that the intensity increased until 350°C and remained fairly constant thereafter. An identical crystal, annealed directly to 550°C developed no such line, as is plotted by the triangles. This slide (11) shows a similar plot for the donor dopant (phosphorous). It also increased in intensity at the higher annealing temperatures.

The following three overheads present data on the shifting of the observed line in field position at different annealing temperatures. Again, the temperature of anneal is plotted on the horizontal axis. The g-shift is plotted on the vertical axis. It is plotted as the number of gauss upfield from the 3rd manganese line where the sample line was found. A shift in the sample line to higher field was observed in all samples, but the increase did not always occur in the same way.

This slide (12) shows data for both boron doped crystals. The line position remained fairly constant until the anneals at 450°C and 550°C. Note again the close correspondence between these two samples. This slide (13) shows a similar plot for gallium. Here the increase occured during the 250°C and 350°C anneals and leveled off at higher temperature anneals. This slide (14) shows the data for phosphorous, and here most of the increase in field position occured at lower temperature anneals, also.

Within experimental uncertainty, the g-values of all four acceptor crystals at room temperature are the same. Hence it is likely that the same defect in all four samples causes the observed line. This would lead one to suspect the line is caused by conduction electrons, although the known g-value is lower than the g-value observed.

Another possibility is dangling bonds due to internal voids. The known g-value of dangling bonds is slightly lower at 2.0055, (vs 2.0059) and the expected width of such a line is 6-7 gauss, which agrees very well with our data.

The g-values for the donor-doped silicon are much smaller, at about 2.0026. This is fairly close to the g-value of the so-called P1 center, a pentavacancy cluster at 2.0020. P1 grows above about 170°C following the liberation of vacancies from the P-3 centers. The P1 center anneals out at about 500°C - 600°C. This is consistent with our data.

Annealing of acceptors in general lowered g down to the donor level value. This was very similar to the shift in the line during anneals of electron-irradiated, indium doped silicon, which was examined in an earlier study. There the line shifted from g = 2.0058 to g = 2.0026.

A great many defects in silicon have been observed; for example Corbett has identified over 50 such defects, most near g = 2. This makes identification of a line in this range difficult. Further anneals on these samples and annealing experiments on other silicon samples will be done to investigate further the above possibilities. Thank you.

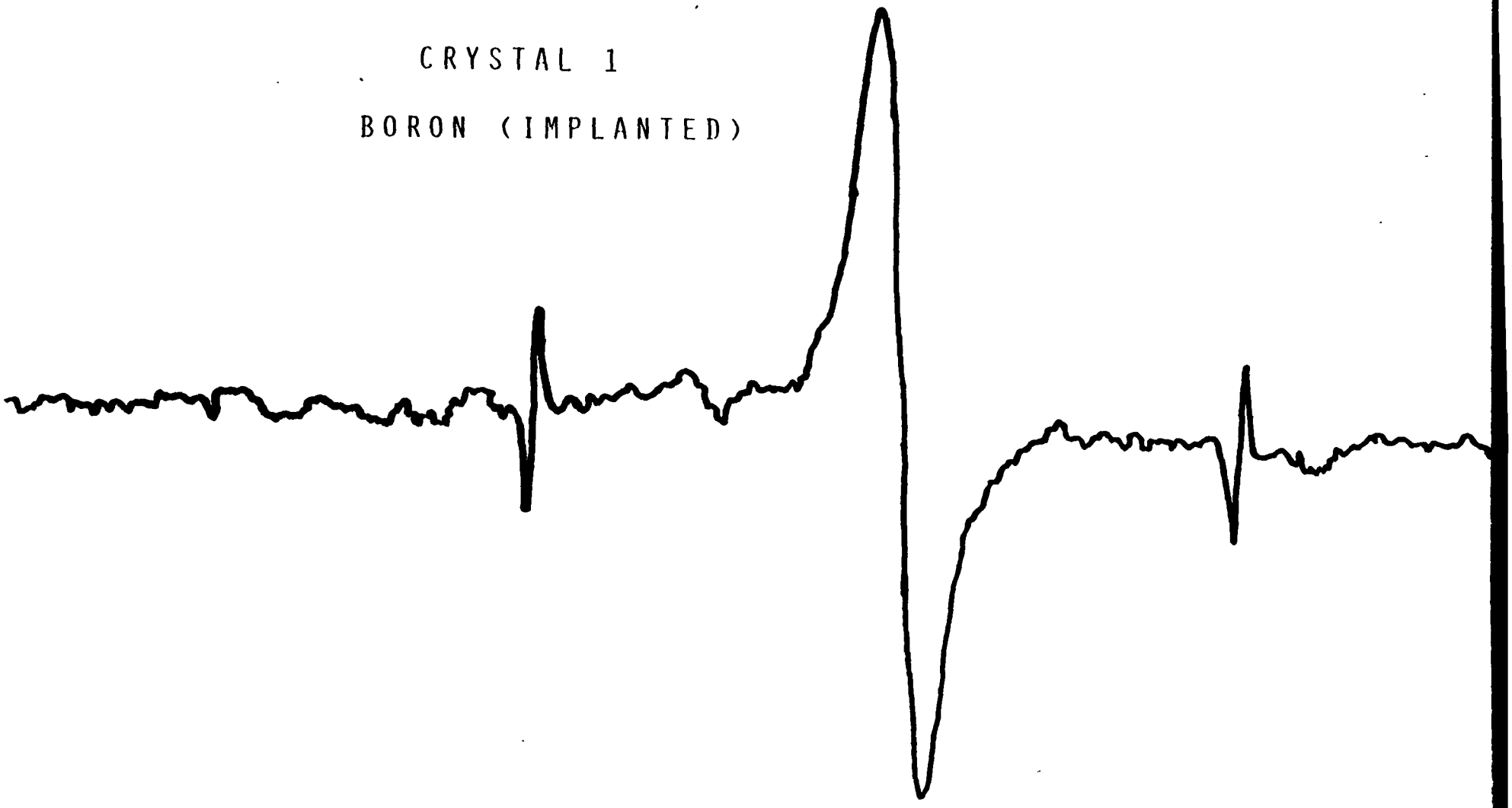
"E P R Measurements in Silicon Doped with Boron, Gallium or Indium Acceptors"

SILICON SAMPLES

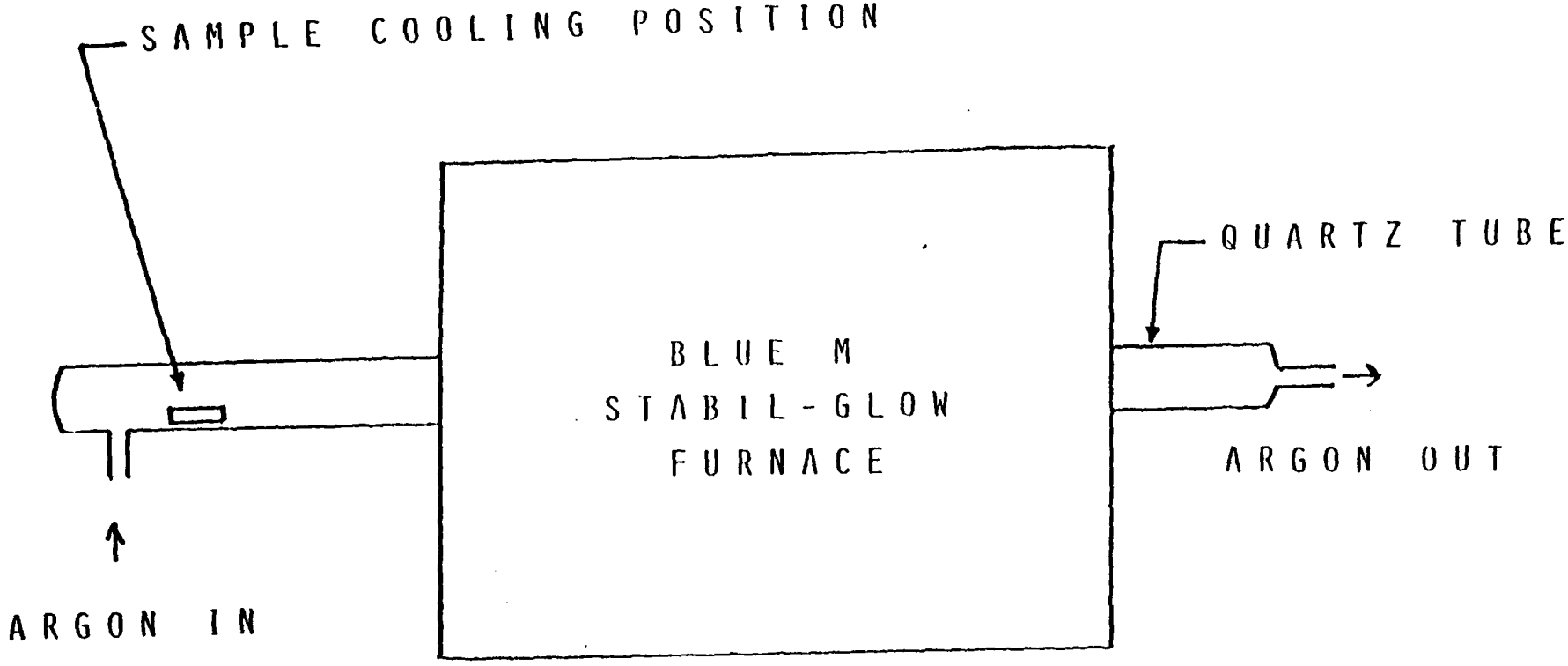
CRYSTAL	DOPANT	PREPARATION
1	BORON	IMPLANTED THEN FLOAT-ZONED
2	BORON	DIBORANE GAS DURING FLOAT-ZONING
3	GALLIUM	FLOAT-ZONED
4	INDIUM	FLOAT-ZONED
5	NONE	FLOAT-ZONED
6	PHOSPHORUS (DONOR)	NEUTRON TRANSMUTATION DOPED

CRYSTAL 1

BORON (IMPLANTED)

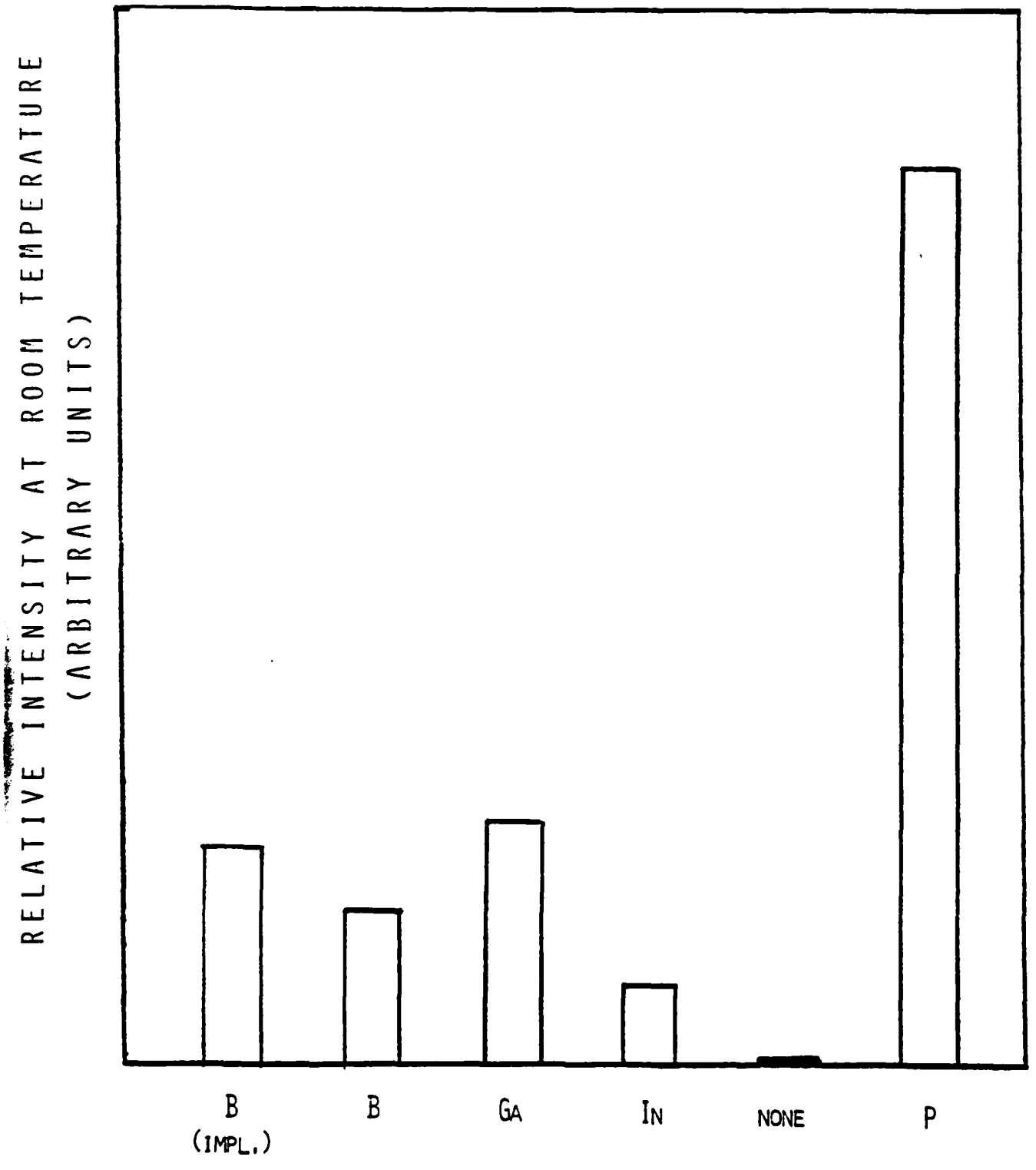


SLIDE 3

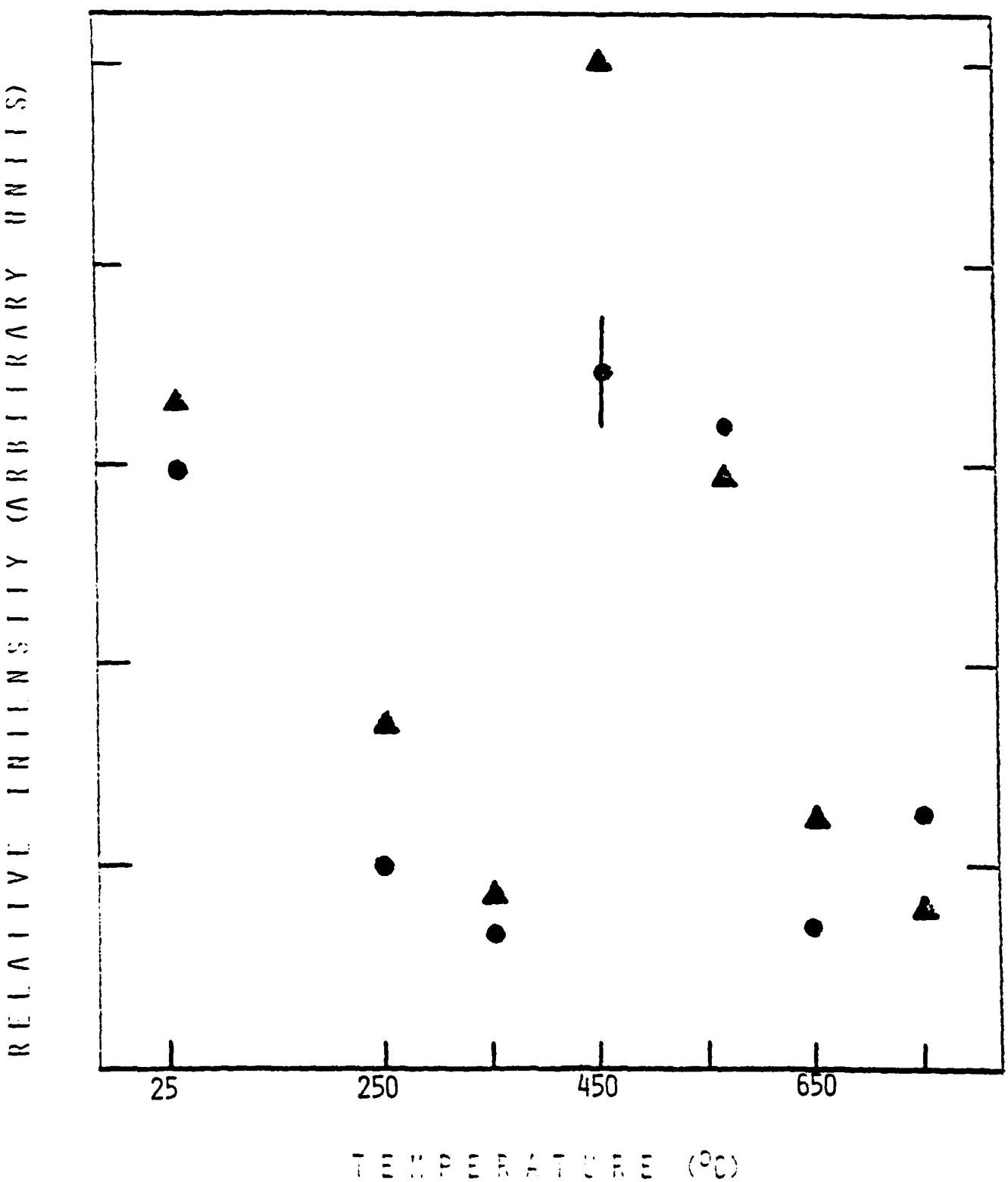

SAMPLE COOLING POSITION
QUARTZ TUBE
BLUE M
STABIL-GLOW
FURNACE
ARGON OUT
ARGON IN

SLIDE 4

CRYSTAL	DOPANT	g-VALUE
1	B (IMPLANTED)	2.0060 ± .0002
2	B	2.0059 ± .0002
3	Ga	2.0059 ± .0002
4	In	2.0058 ± .0002
5	NONE	
6	P	2.0026 ± .0002

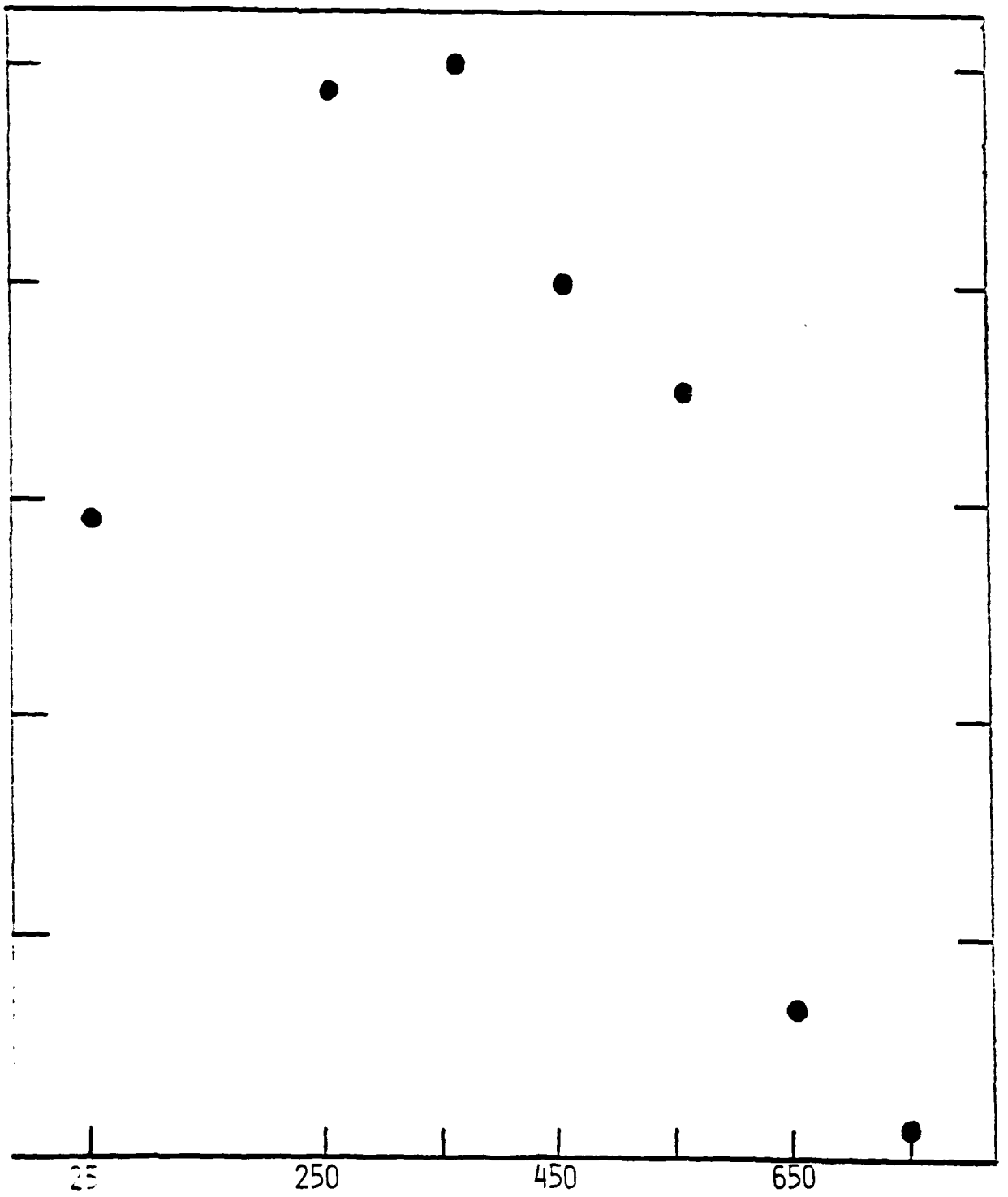

RELATIVE INTENSITY AT ROOM TEMPERATURE
(ARBITRARY UNITS)
B
(IMPL.)
B
GA
IN
NONE
P
DOPANT

SLIDE 7


▲ CRYSTAL 1 - BORON (IMPLANTED)
● CRYSTAL 2 - BORON
RELATIVE INTENSITY (ARBITRARY UNITS)
25
250
450
650
TEMPERATURE (°C)

SLIDE 8

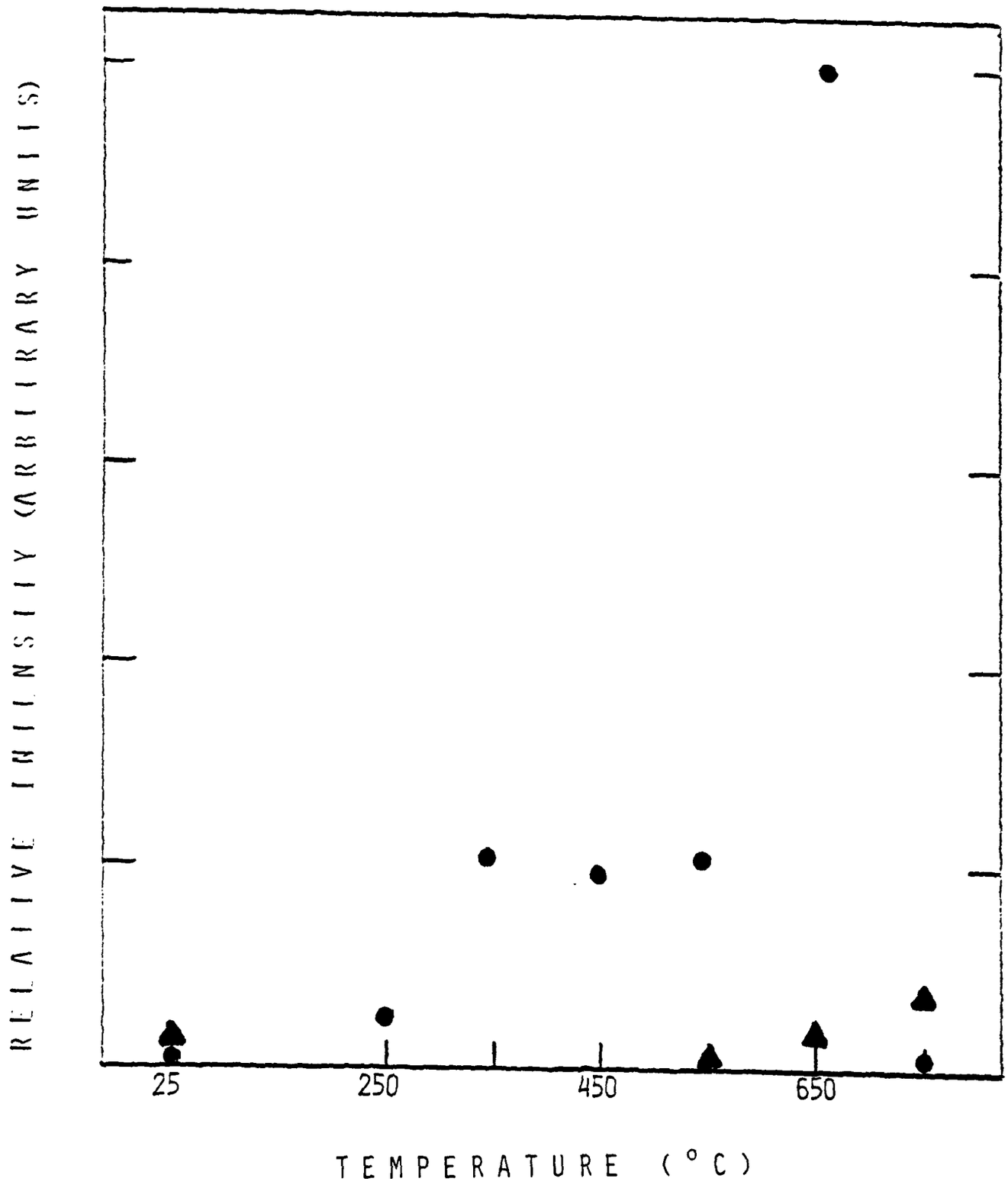
CRYSTAL 3 - GALLIUM



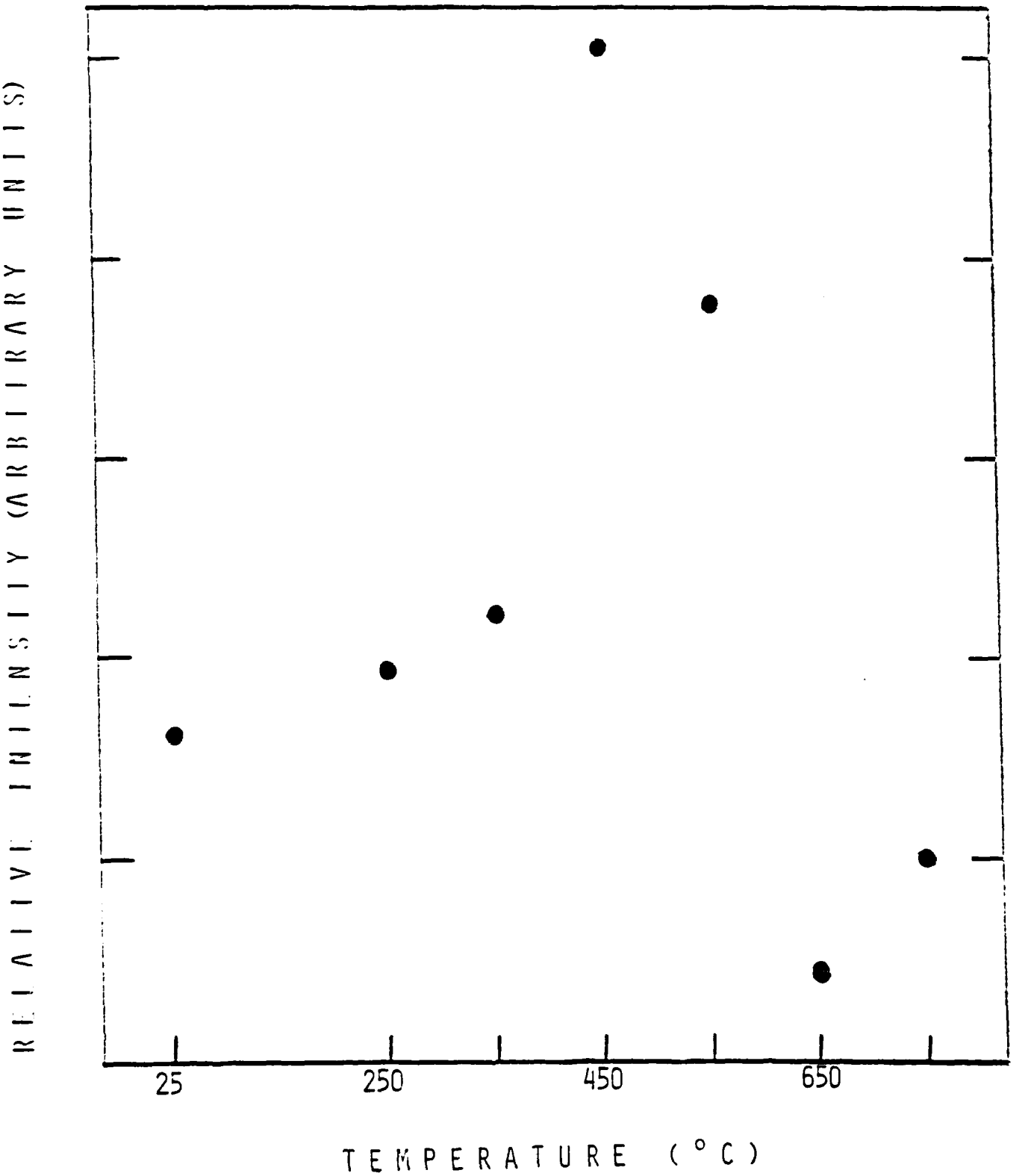
SLIDE 9

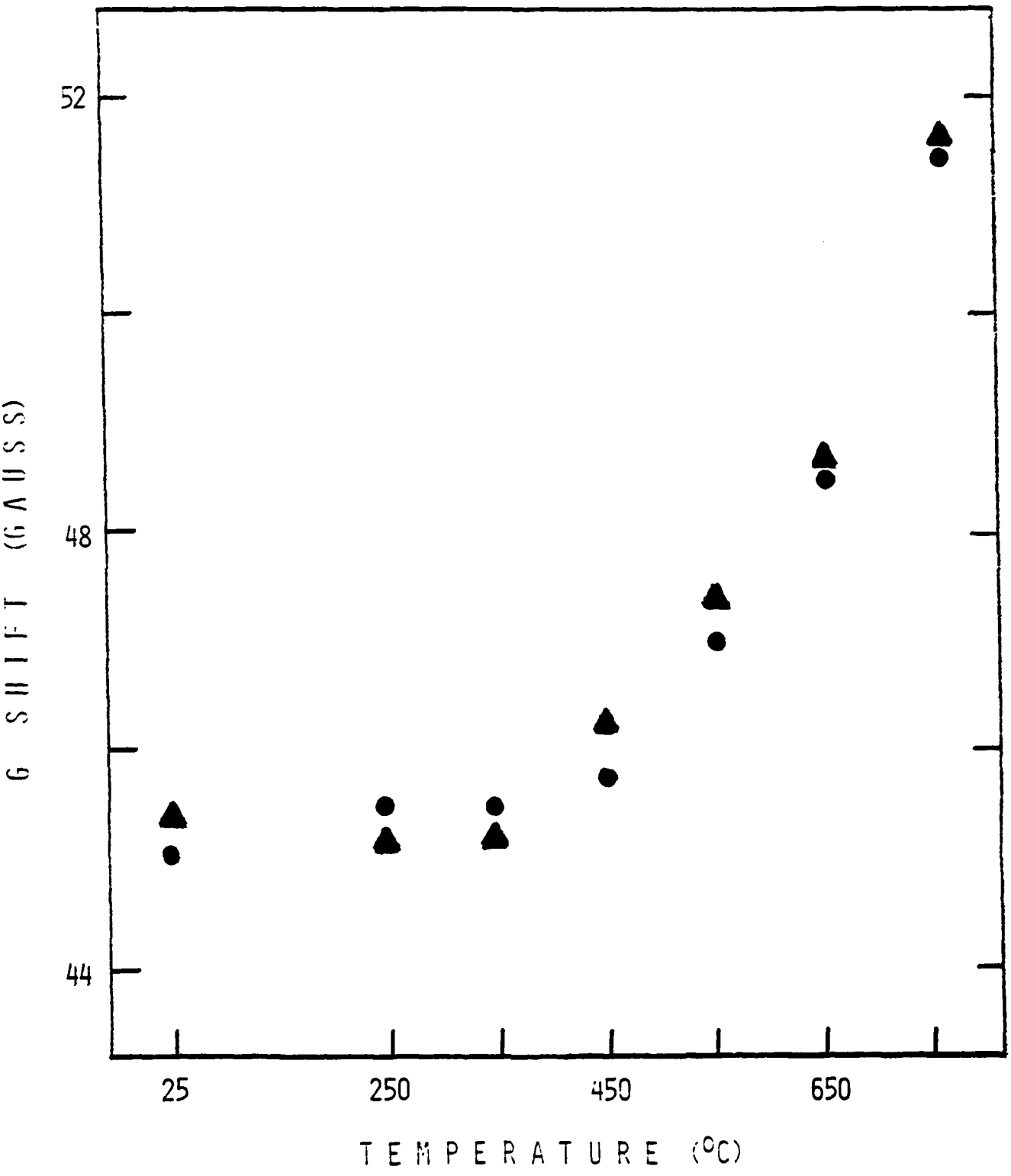
CRYSTAL 4 - INDIUM
RELATIVE INTENSITY (ARBITRARY UNITS)
TEMPERATURE (°C)
25
250
550
850
1050
250
550
750
250
550
750

CRYSTAL 5 - NO DOPANT

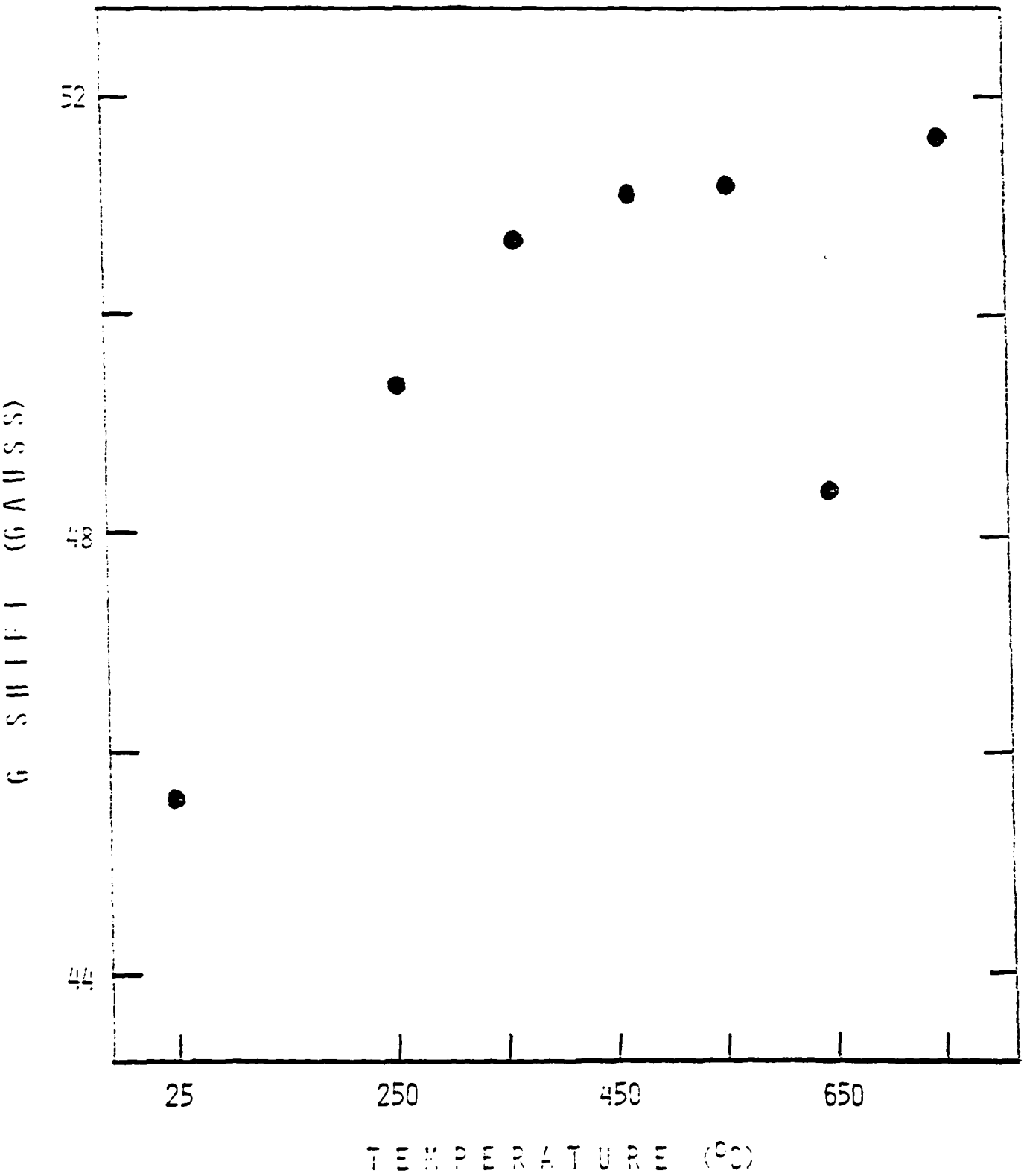


CRYSTAL 6 - PHOSPHOROUS




▲ CRYSTAL 1 - BORON (IMPLANTED)
● CRYSTAL 2 - BORON
52
48
44
G SHIFT (GAUSS)
25
250
450
650
TEMPERATURE (°C)

CRYSTAL 3 - GALLIUM



CRYSTAL 6 - PHOSPHOROUS